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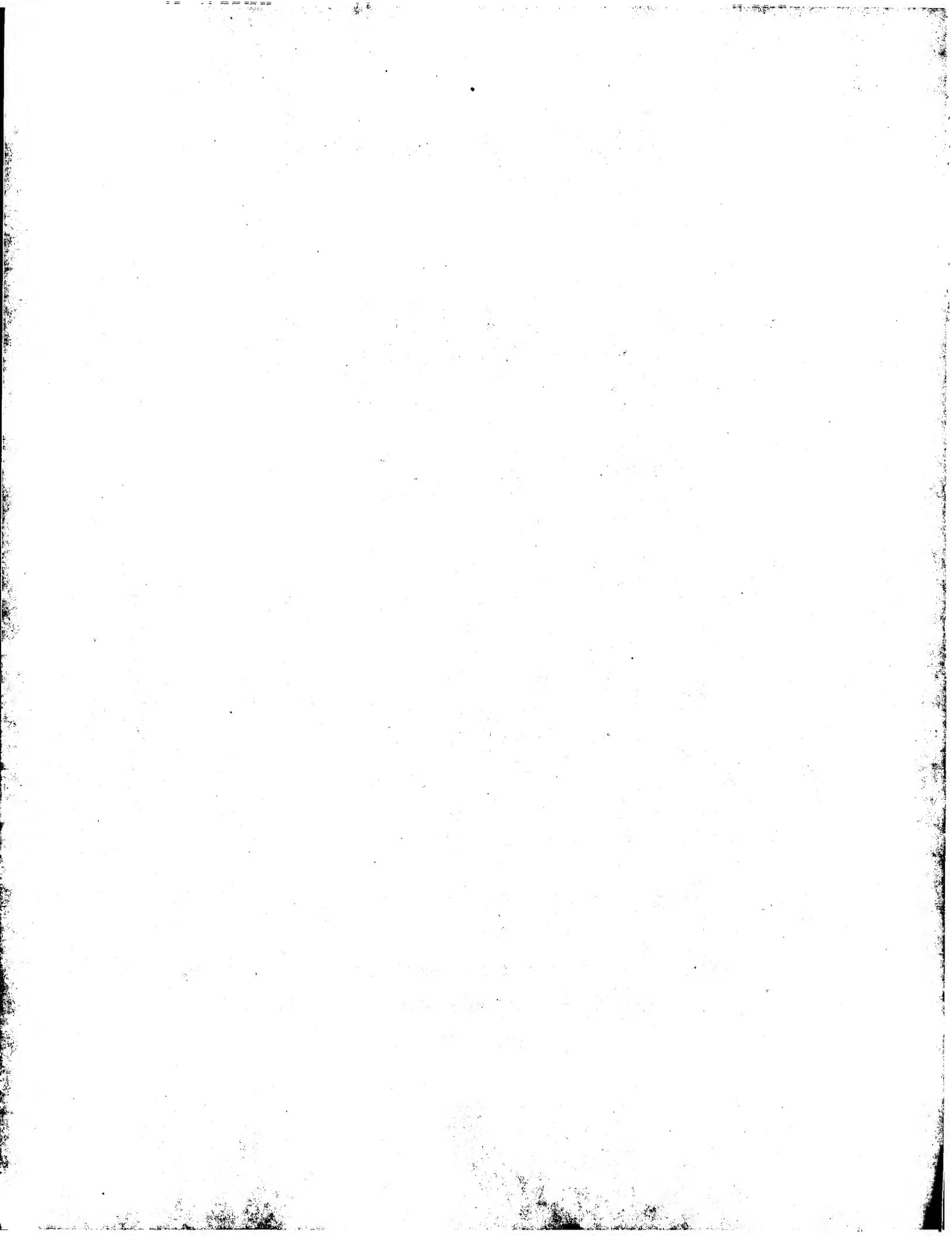
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**PART I: SYNTHESSES AND CHARACTERIZATION OF
POLY(2-DECYLTHIENO[3,4-b]THIOPHENE),
A LOW BANDGAP CONDUCTING
POLYMER**

**PART II: FORMATION AND TRAPPING OF
METHOXY(METHOXY-
CARBONYL)KETENE**

by
XIAOMIN GU

Presented to Faculty of the Graduate School of
The University of Texas at Arlington in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT ARLINGTON

December 1995

To my husband, Jiping Wang, and my son Muzhou (Mitchell) Wang
for their love and support

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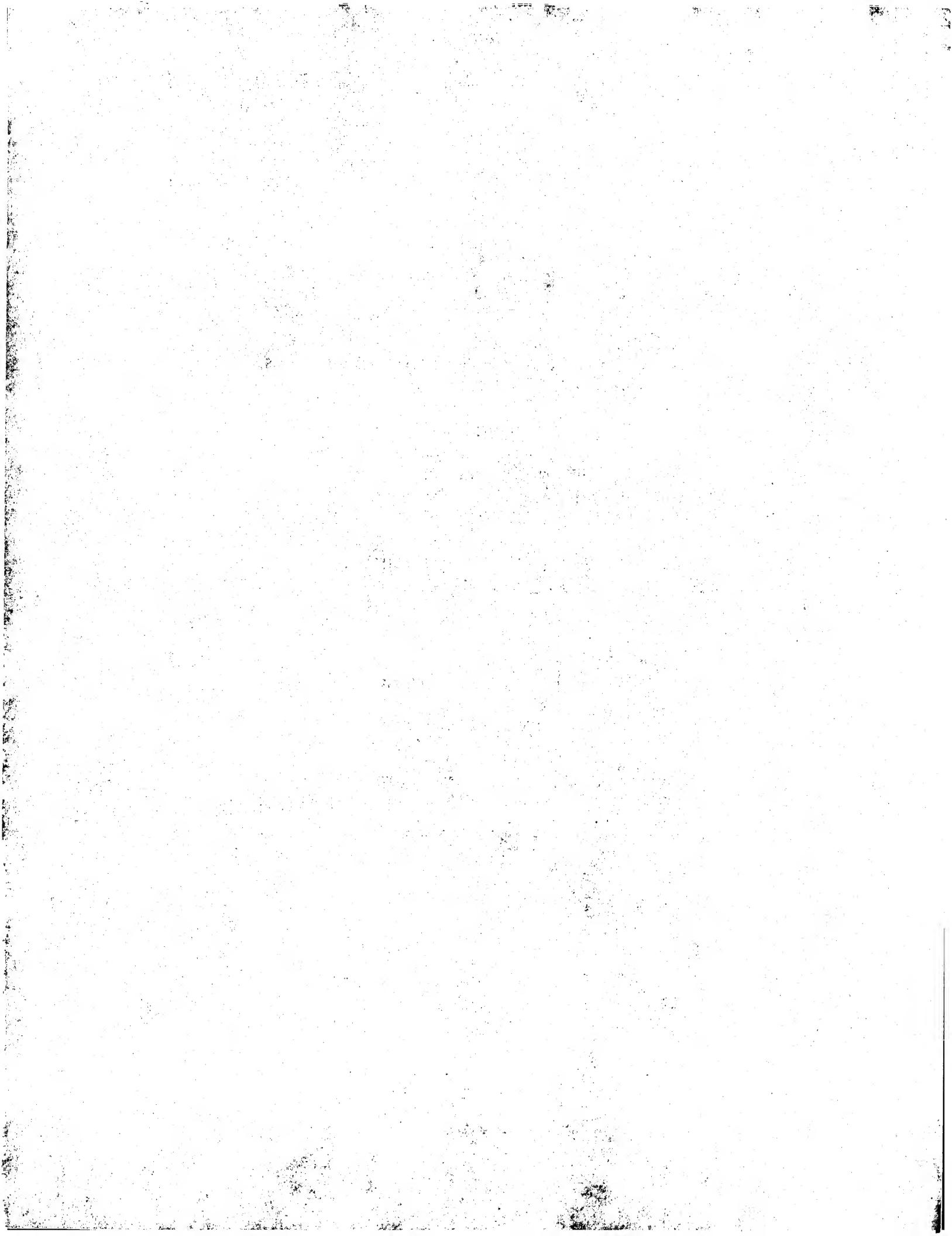


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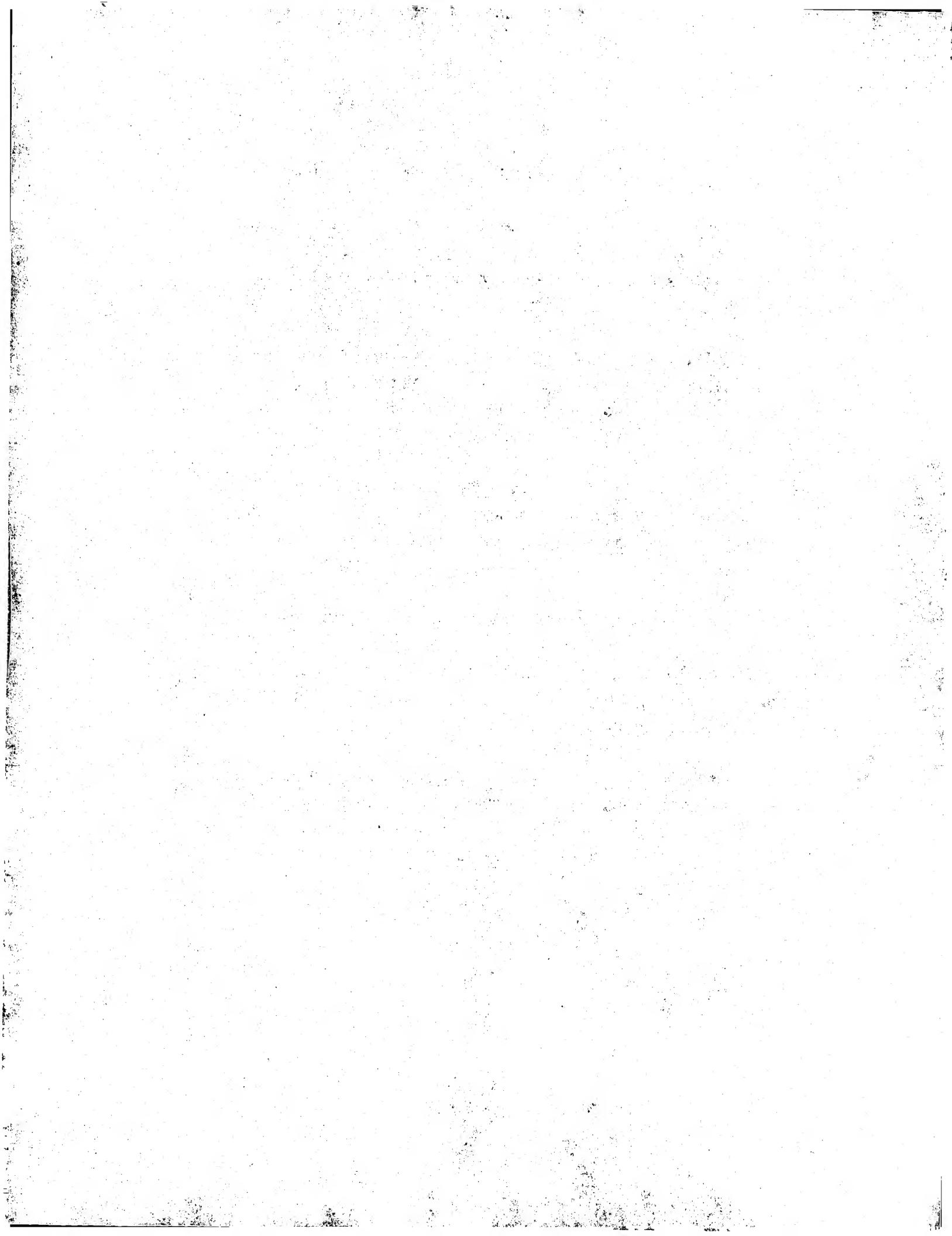
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OF METHOXY(METHOXY-
CARBONYL)KETENE

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August 14, 1995

ABSTRACT

Part I: Syntheses and Characterization of
Poly(2-decylthieno[3,4-b]thiophene,
A Low Bandgap Conducting
Polymer

Part II: Formation and Trapping of
Methoxy(methoxy-
carbonyl)ketene

Publication No._____

Xiaomin Gu, Ph.D.

The University of Texas at Arlington, 1995

Supervising Professor: Martin Pomerantz

Part I: A new low bandgap conducting polymer, poly(2-decylthieno[3,4-b]thiophene) (2.1), has been synthesized by two different synthetic routes. Polymerization via 4,6-dichloro-2-decylthieno[3,4-b]thiophene (2.19) using a Ni(0) complex yielded a polymer which was only slightly soluble in CHCl₃ and THF. Electrical conductivity of the pressed pellets was 1.4×10^{-6} S cm⁻¹ before doping and 2.9×10^{-6} S cm⁻¹ after doping with NOBF₄. Polymerization via 2-decylthieno[3,4-b]thiophene (2.33) using a FeCl₃ oxidative polymerization method yielded a polymer which was soluble in CHCl₃ and THF. The molecular weight was M_n = 3.0×10^4 g mol⁻¹ determined by GPC using polystyrene standards. The bandgap calculated from the absorption maximum was 1.68 eV (1.2 eV from the band edge), which was very close to the bandgap (1.5 -1.6 eV) from theoretical

calculations. Electrical conductivities of the polymer films cast from CHCl₃ solution were 2.2 x 10⁻⁵ S cm⁻¹ without doping, 8.8 x 10⁻³ S cm⁻¹ after doping with I₂ and 7.2 x 10⁻² S cm⁻¹ after doping with FeCl₃ in CH₃OH.

Part II: Two dimers, dimer **9**, 2,5-dimethoxy-2,4-bis(methoxycarbonyl)-2,3-dihydrofuran-3-one, and dimer **10**, 2,4-dimethoxy-2,3-bis(methoxycarbonyl)-3-buten-4-olate, are formed in the thermal decomposition of dimethyl diazomalonate (**8**). **9** was postulated to result from the reaction of methoxy(methoxy-carbonyl)ketene (**11**) (formed from bis(methoxycarbonyl)carbene (**12**) by Wolff rearrangement) with the carbene **12** and **10** was suggested to be the product of **11** and **8**. Ketene **11** was independently prepared by dehydrohalogenation of methyl 3-chloro-2-methoxy-3-oxopropanoate (**13**) but attempts to observe reaction with **8** were unsuccessful. Trapping of the ketene **11** with cyclopentadiene produced **16** whose structure was proven by X-ray crystallography and whose stereochemistry is different from the prediction by the Woodward-Hoffmann rules but in agreement with recent theoretical calculations.

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**PART I: SYNTHESSES AND CHARACTERIZATION OF
POLY(2-DECYLTHIENO[3,4-b]THIOPHENE),
A LOW BANDGAP CONDUCTING
POLYMER**

CHAPTER 1

INTRODUCTION

Since the discovery that polyacetylene becomes highly conducting upon oxidation,¹ a number of polymer systems have been found to exhibit electronically conducting properties. The electrical conductivity σ in a system can be described by equation 1.1, where n is the total

$$\sigma = nq\mu \quad (1.1)$$

number of free-carriers, q is the charge on the carriers, and μ is the mobility of the carriers.² An overlapping set of molecular orbitals in conjugated organic polymers provides reasonable carrier mobility along the polymer chain. However, conjugated organic polymers in their neutral state are best described as electrical insulators although they have a relatively higher electrical conductivity than that of non-conjugated organic polymers (Figure 1.1). The doping (oxidation or reduction) of conjugated organic polymers generates high electrical conductivities primarily by increasing the number of charge carriers. For example, polythiophene is oxidized by the removal of an electron, thereby producing a radical cation (polaron) on the chain (Figure 1.2). A second oxidation can occur directly on the polaron to form the dicationic bipolaron. It is these charged defects which are introduced along the polymer backbone by partial oxidation (removal of electrons) or partial reduction (addition of electrons) that give the conducting properties to conjugated organic polymers.

Organic conducting polymers have a highly anisotropic quasi-one-dimensional structure similar to that of organic charge-transfer complexes. In charge-transfer salts, conductivity is greater along the stacking direction (molecules stack on top of each other using π - π overlap

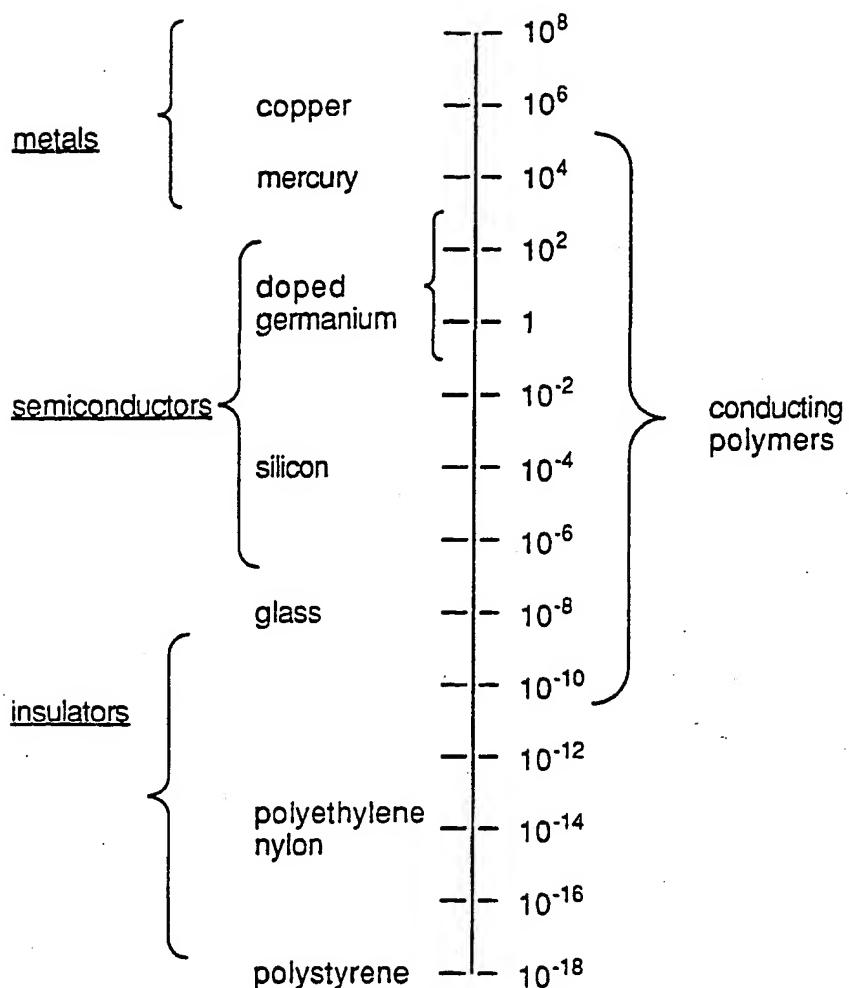


Figure 1.1. Electrical conductivity range of metals, semiconductors, insulators and conducting polymers

between large, polarizable atoms such as sulfur or successive molecules). In conducting polymers, conductivity is higher along the chain direction through $\pi-\pi$ overlap between successive monomers.

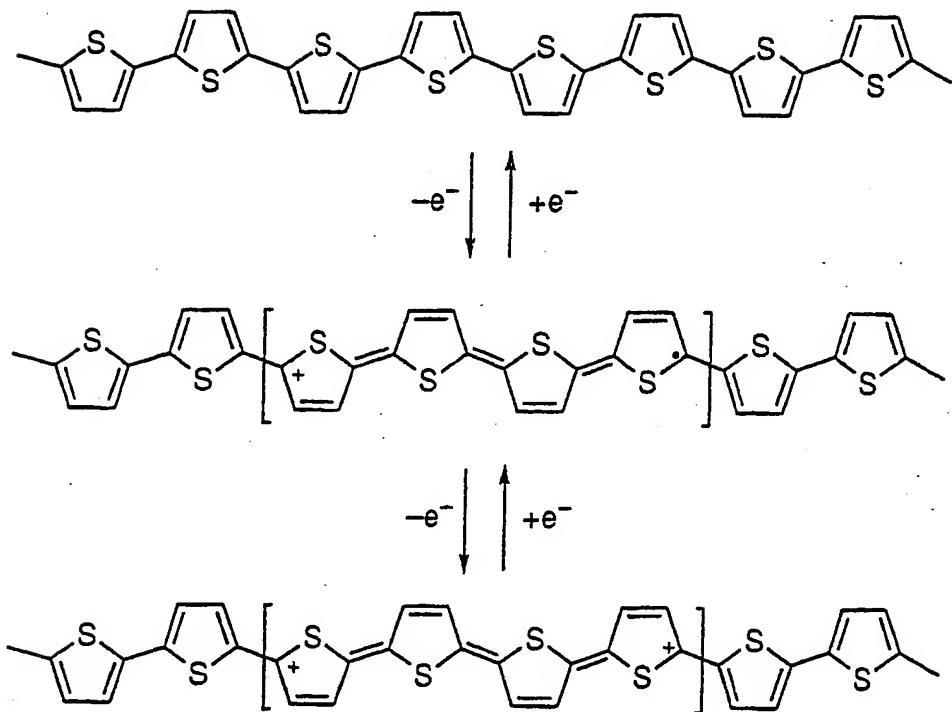


Figure 1.2. Formation of polaron and bipolaron states on a polythiophene chain

The bandgap (E_g) of conjugated polymers represents the interband energy gap from the valence band to the conduction band shown schematically in Figure 1.3. E_g is usually measured by the absorption bandedge in the UV-vis-NIR spectrum although the absorption maximum is sometimes used as the E_g of conjugated polymers. E_g can also be measured by the energy difference between oxidation and reduction potentials. When a conjugated polymer is doped, the positive charge on the polymer chain results in a deformation of the geometric structure, yielding self-localized states with energy localized levels within the energy gap, E_g . As the doping process is increased to the point of saturation, the density of these localized states becomes large enough to overlap in space with one another. The result is the formation

of a 'lattice' of localized states which produces bands within the previous energy gap. Diagrams for the relevant portion of the energy band structures for a polaron lattice and a bipolaron lattice are shown in Figure 1.3.³

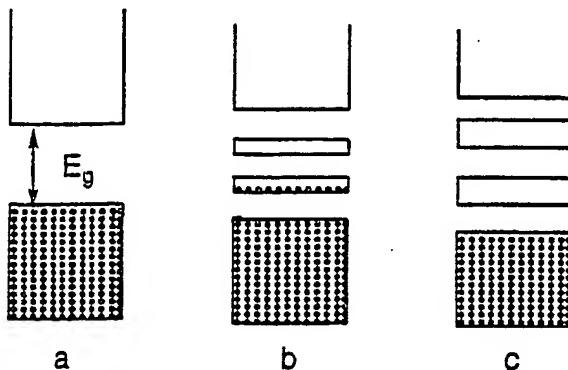


Figure 1.3. Electronic band structure of conjugated polymer
a. neutral state; b. polaron; c. bipolaron.

Conjugated polymers are currently attracting much interest as a new class of electronic materials for a wide variety of applications. Much study has been devoted to the development of conjugated polymers on account of their novel electrical, electrochemical and optical properties which lead to their potential use as electronically conducting materials, electroluminescent materials and third-order non-linear optical (NLO) materials. The photoluminescence and electroluminescence of these polymers have been extensively studied for the realization of light-emitting devices and large-area multicolor displays. Potential industrial applications of conducting polymers are listed in Table 1.1.⁴⁻¹² The promise of conducting polymers is to combine the chemical, mechanical, and processing properties of the traditional polymers with the electric behavior of semiconductors and metals. Their advantages over metallic materials, such as ease of fabrication, light weight and chemical inertness, make them a new type of interesting electronic materials.

Table 1.1. Potential Applications of Conducting Polymers
(* Real Commercial Applications)

Cable Shielding

* Capacitors

Controlled-Release Medicine Systems

Electro-Robotics

Electrochromic Smart-Windows

Electroluminescent Flexible LED's

Electromagnetic Shielding

Electron-Beam Resist

* Electrostatic Control

Gas Separation Membranes

Nonlinear Optics

* Rechargeable Batteries

* Sensors

* Conductive Textiles

Biotechnology and Tissues

Engineering Applications

Figure 1.4 summarizes the parent structures of highly conjugated polymers which have drawn the most attention in the past few years. These polymers and their derivatives cover most known electronically conductive polymers.

1.1 Polythiophenes

Polythiophene and its derivatives continue to be an active research area in the development of new electronic materials and are useful tools for understanding the chemistry

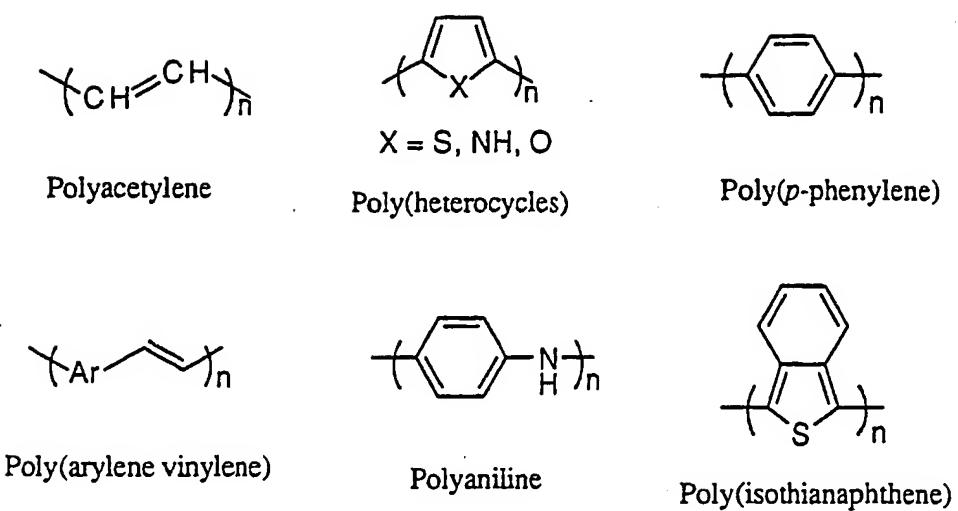


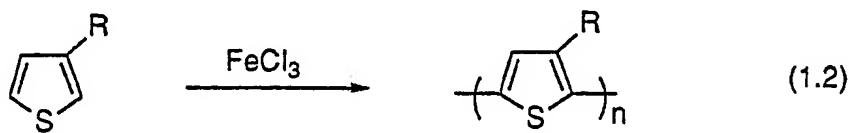
Figure 1.4. Parent structures of the most widely studied electronically conductive polymers

and physics of conducting polymers.¹³⁻¹⁷ They are the first examples of conducting polymers that are environmentally stable both in their neutral and in their conducting states. Similar to most fully conjugated polymers, the conjugated structures of polythiophenes tend to yield relatively stiff chains with little flexibility and with relatively strong interchain attractive interaction, leaving them insoluble and nonprocessable. By substituting long flexible chains in the 3-position of the thiophene ring, the chain interactions can be decreased and high processability (soluble and fusible) can be achieved with a minimal effect on the properties derived from the conjugation of the backbone.¹⁸ The initial preparation of soluble poly(3-alkylthiophenes) was done in 1985 by Elsenbaumer et al.,¹⁹ and several other research groups also reported the synthesis of similar polymers in 1986.²⁰⁻²² With the introduction of the poly(3-alkylthiophenes), increased processability has allowed for the formation of films and fibers of the polythiophene class of conducting polymers through both melt- and solution-processing routes. The electrical, mechanical, and optical properties as a function of the alkyl side-chain length have been investigated.²³⁻²⁵ The alkyl side-chain lengths of 6, 8 and 12

carbon atoms were the most widely chosen since they were expected to be long enough to induce solubility and fusibility but not so long that the side-chains would crystallize in the solid state.¹⁸

Polythiophene and its derivatives can be synthesized chemically or electrochemically. For electrochemical polymerization, the oxidative anodic electropolymerization of the monomer is the most convenient and most widely used method. The electrochemically synthesized polythiophene is obtained in the doped conducting state and can be chemically or electrochemically undoped to its neutral state. Compared to other chemical and electrochemical methods, the anodic electropolymerization of the monomer has several advantages such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface, and easy control of the film thickness by the deposition charge.¹³

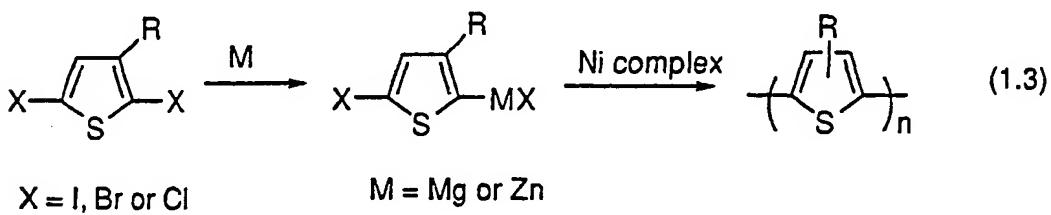
The Lewis-acid-induced (generally using FeCl₃) polymerization is a widely used polymer preparation method for the synthesis of polythiophene and its derivatives (equation 1.2). This procedure, which was first reported in 1984 by Yoshino et al.,²⁶ has become an



excellent method for preparation of poly(3-alkylthiophenes) and other thiophene-based polymers.¹⁸ This chemical oxidation polymerization produces the polymer in the oxidized (doped) conducting state, which is the same as the electrochemically synthesized polymer. The polymer can then be dedoped by NH₃, hydrazine, etc. to its neutral state. Most other chemically synthesized polymers are produced in their undoped insulating state and can be doped chemically or electrochemically to their conducting state. Instead of poly(3-alkylthiophenes), the FeCl₃ oxidation polymerization can be also used to prepare polythiophene

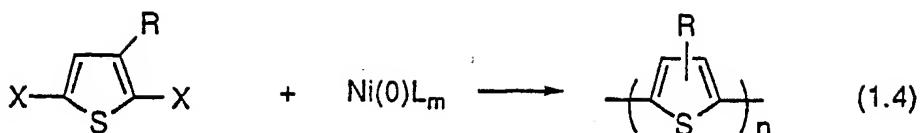
derivatives with other side chains such as urethane side chains²⁷ or 3,4-substituted ethylenedithia and ethylenedioxo side groups.²⁸

The organometallic dehalogenation polycondensation of dihalo-monomers by nickel-catalyzed processes has been developed as one of the major polymerization methods for polythiophene and its derivatives (equation 1.3).^{19,21,29} The chemical coupling polymerization



involving the nickel-catalyzed coupling of the mono-Grignard reagent is a good example of the organometallic dehalogenation polycondensation. Among the transition metal complexes, nickel compounds serve as the best catalyst for this coupling reaction.³⁰ The mono-organozinc compound is a useful alternative reagent to the Grignard reagent in this polycondensation.³¹ In the case of polythiophenes prepared by chemical and electrochemical oxidative polymerization, the polymers may contain not only the 2,5-bonded thiophene units but also the 2,4-bonded thiophene units because the β C-H bond in thiophene is also active in the oxidative polymerization.^{32,33} On the other hand, in the case of polythiophenes prepared by the organometallic dehalogenation polymerization, only the C-X bond is active and the polymers are considered to be constituted only of monomer units bonded at the C-X bond.^{34,35}

In addition to the coupling reactions between a Grignard reagent and an organic halide, C-C coupling of organic halides using a zero-valent nickel complex itself as a dehalogenation reagent has been developed to prepare the polythiophenes (equation 1.4).³⁶⁻³⁸

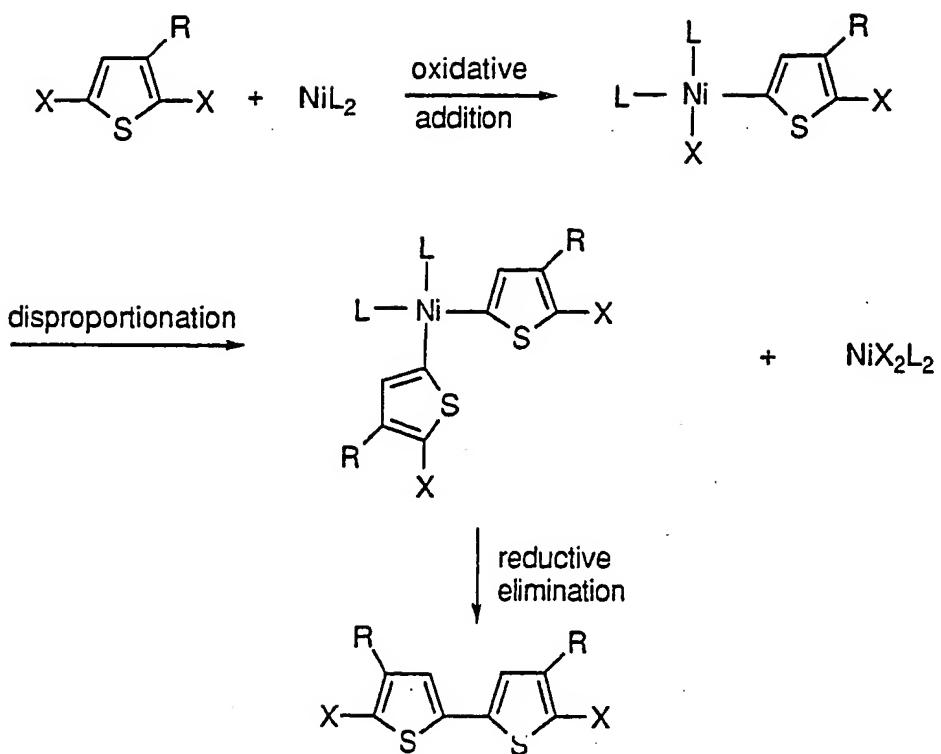


$X = I, Br \text{ or } Cl$

Since this reaction proceeds under mild conditions, it can be applied to a wide range of aromatic compounds, especially to those which are difficult to prepare by dehalogenation polycondensation involving Grignard reagents. This is the most direct and simple reaction among the transition metal promoted coupling reactions and is expected to provide a versatile means for molecular design and synthesis of electrically conducting polymers. Compared with the coupling reaction (equation 1.3) involving a Grignard reagent where a Ni(II) complex is used as a catalyst, a stoichiometric amount of Ni(0) complex must be used in this reaction. The basic reactions involved in this coupling polymerization are oxidative addition, disproportionation, and reductive elimination (Scheme 1.1).³⁶⁻³⁸

Among the zero-valent nickel complexes such as $Ni(CO)_4$, $Ni(PPh_3)_4$ and $Ni(COD)_2$ ($COD = 1,5\text{-cyclooctadiene}$), $Ni(COD)_2$ in the presence of 2,2'-bipyridine (bpy) or triphenylphosphine (PPh_3) as the auxiliary ligand in dimethylformamide (DMF) gives the best yield of polythiophene and its derivatives.³⁸ It is reported that tertiary phosphine ligands such as PPh_3 usually afford the trans-Ni(II) complex, whereas the bidentate bpy ligand affords the cis-Ni(II) complex.^{39,40} The reductive elimination usually proceeds more easily in the cis-type complex than in the trans-type complex, and the disproportionation reaction involving exchange of the anionic ligands X and ArX may also go more easily in the cis-type complex.^{41,42}

Scheme 1.1



The dehalogenation coupling polymerization using a mixture of $\text{Ni}(\text{COD})_2$ and 2,2'-bipyridine in DMF proceeds very smoothly at 60 °C, whereas the reaction proceeds much more slowly at room temperature.³¹ Higher temperatures (e.g., 100 °C) may cause decomposition of the Ni complex and reduce the polymer yield due to the formation of side-products. For example, the polymerization of 3-octyl-2,5-diiodothiophene at 60 °C gave the polymer with a negligible content of iodine in 95% yield. However, the polymerization at 30 °C gave the polymer containing 2% iodine due to the terminal units, and the polymer obtained at 100 °C gave a lower yield of 80%. Lower polymer yield was also obtained when toluene was used as the solvent instead of DMF, presumably due to greater difficulty of disproportionation of the supposed intermediate $\text{NiX}(\text{Ar})(\text{bpy})$ complex in nonpolar solvents like toluene.³⁷ Use of triphenylphosphine gave the polymer with considerably lower molecular weight.

The poly(3-octylthiophene) and poly(3-dodecylthiophene) obtained by using $\text{Ni}(\text{COD})_2$ have considerably lower solubility than the poly(3-hexylthiophene).³¹ The low solubility of poly(3-dodecylthiophene) is in contrast to the high solubility of the corresponding polymer prepared by chemical oxidation of 3-dodecylthiophene with FeCl_3 . No reason was reported for this reduction of solubility.

Direct polymerization of dihalobenzenes by zero-valent nickel reagents has the following two disadvantages compared to the coupling reaction involving Grignard reagents: (1) stoichiometric amounts of expensive $\text{Ni}(0)$ complexes are necessary and (2) the very air-sensitive reagents of $\text{Ni}(0)$ complexes require careful handling. In order to overcome these two problems, zinc can be used as a reducing reagent for preparing $\text{Ni}(0)$ complexes from $\text{Ni}(\text{II})$ complexes such as NiCl_2 and NiBr_2 .^{43,44} In this case, only a catalytic amount of $\text{Ni}(\text{II})$ complex with excess reducing reagent is needed to make the polythiophenes instead of a stoichiometric amount of expensive $\text{Ni}(0)$ complex (equation 1.4). During the reaction, the by-product of the disproportionation, NiX_2L_m can be reduced by the zinc to the $\text{Ni}(0)$ complex which can reenter the reaction to form the oxidative addition product.

The Ullmann coupling reaction has very recently been successfully used to prepare 3-substituted polythiophenes with the electron withdrawing groups such as esters.^{45,46} The treatment of the dihalides with freshly prepared copper powder in DMF at 145-150 °C gave good yields of poly(alkyl thiophene-3-carboxylates). It should be noted that the polythiophenes with electron withdrawing substituents directly attached to the thiophene ring are hard to prepare by oxidative polymerization or organometallic coupling reaction because the electron withdrawing groups decrease the reactivity of the thiophene ring.^{47,48}

The 3-substituted polythiophenes prepared by the three major polymerization routes described above have various degrees of regioregularity due to the formation of head-to-head (H-H), head-to-tail (H-T), and tail-to-tail (T-T) configurational isomers. (Figure 1.5)

Regioregularity refers to the structural regularity of H-H (2,2'- coupling), H-T (2,5'- coupling), and T-T (5,5'- coupling) isomers in the polymer main chain. The relative predominance of one coupling reaction over the other to form a particular isomer is said to be regioselective, whereas it is termed regiospecific if only a single isomer is present.⁴⁹

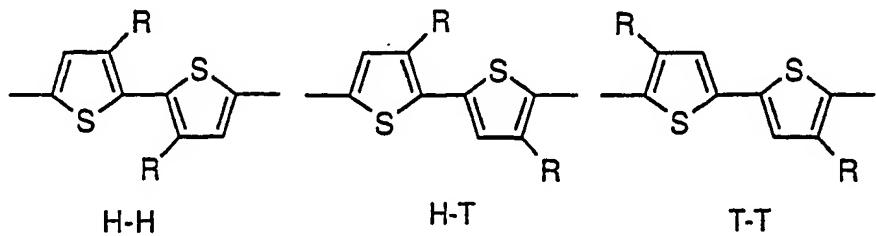


Figure 1.5. The possible couplings of 3-substituted thiophenes

The regularity and structure of the 3-substituted polythiophenes can be readily studied by nuclear magnetic resonance (NMR) spectroscopy.⁵⁰⁻⁵² The random polymerization produces the polymer with four different thiophene rings because of three different couplings at 2,5 position of a 3-substituted thiophene (Figure 1.6). In the ¹H NMR spectrum, the four aromatic proton peaks are assigned to the isolated 4-proton on the successive thiophene rings and arise from different configurations. The ¹³C NMR spectrum should show sixteen different aromatic carbon atoms for the regiorandom 3-substituted polythiophenes. For the structurally homogeneous head-to-tail coupling 3-substituted polythiophenes, there is only one aromatic proton peak in the ¹H NMR spectrum and 4 aromatic peaks in the ¹³C NMR spectrum.

It is obvious that head-to-head linkages can cause defects in the conjugated chain due to steric interactions between side groups. The resultant structures must contain large numbers of thiophene rings that are twisted far out of conjugation. A structurally homogeneous head-to-tail arrangement would therefore improve the material's electronic and optical properties.⁵³ A

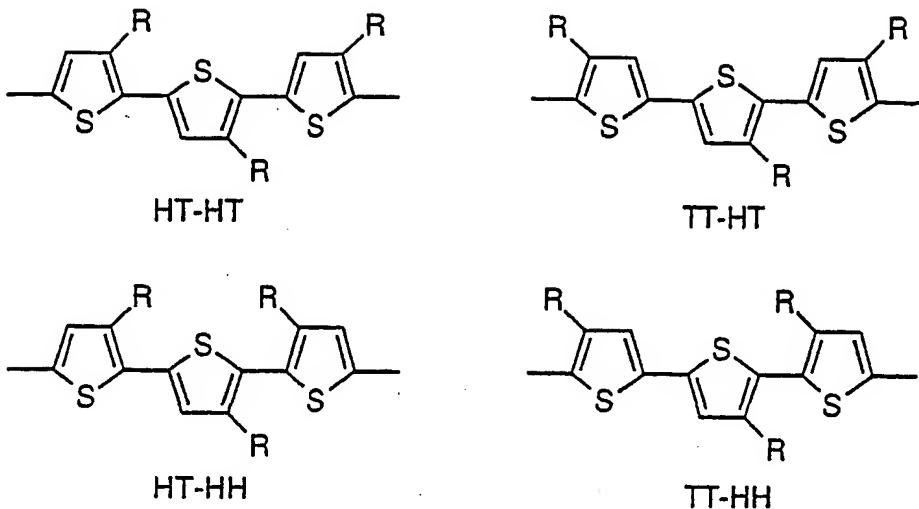


Figure 1.6. Four configurational triads in the regiorandom 3-substituted polythiophenes

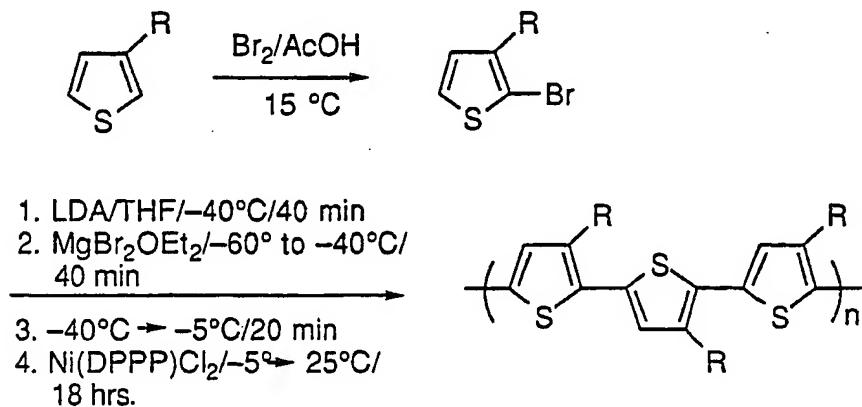
synthesis of this regiospecific polymer requires a synthetic method that gives absolute regiocontrol at each coupling step in the polymerization reaction. A clear indication of the relationship between structural homogeneity and improved electrical and optical properties is also found in Naarmann polyacetylene.⁵⁴

Rieke and coworkers have reported a facile method resulting in the completely regioregular head-to-tail poly(3-alkylthiophenes) using highly reactive zinc and Ni(DPPE)Cl₂ (DPPE = diphenylphosphinoethane) as a catalyst.^{51,55,56} The degree of regioregularity is a function of both the metal and the ligands on the metal. Use of Ni(PPh₃)₄ instead of Ni(DPPE)Cl₂ led to much reduced regioregularity (65:35, HT:HH). Pd(DPPE)Cl₂ (70:30, HT:HH) was not as effective as Ni(DPPE)Cl₂ because of the smaller ionic radius of Ni²⁺ vs Pd²⁺. The regioregular poly(3-alkylthiophenes) exhibit a smaller bandgap (1.7 eV) and a higher intrinsic conductivity (10^{-6} S cm⁻¹ for undoped polymer) than the bandgap (2.0-2.2 eV) and the intrinsic conductivity (10^{-9} - 10^{-10} S cm⁻¹) of regiorandom poly(3-alkylthiophenes). The regioregular polymer also exhibits a large iodine-doped conductivity⁵⁵

(average 1350 S cm^{-1}) compared to about 5 S cm^{-1} for the regiorandom poly(3-alkylthiophenes). The new regioregular polymer has substantially more extended conjugation than any regiorandom polythiophenes.⁵⁷ Recently, this method had been used to prepare poly[3-(alkylthio)thiophenes] with above 90% head-to-tail linkages.⁵⁸

McCullough et al., have also developed a method to prepare regioregular poly(3-alkylthiophenes) with almost 100% head-to-tail couplings (Scheme 1.2).^{52,59,60} The polymerization is performed in a one-flask reaction consisting of metalation of 2-bromo-3-alkylthiophene selectively at the 5-position, followed by trapping the 2-bromo-3-alkyl-5-lithiothiophene with magnesium bromide etherate to afford the Grignard reagent. Subsequent treatment of the Grignard reagent in situ with $\text{Ni}(\text{DPBP})\text{Cl}_2$ ($\text{DPBP} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$) leads to regiochemically defined head-to-tail coupled poly(3-alkylthiophenes).

Scheme 1.2



The poly(3-alkylthiophenes) with regular structure are expected to be highly ordered and therefore exhibit improved electrical conductivity compared to the classical poly(3-alkylthiophenes) which have a large number of defects due to the random coupling at the 2,5 positions of the thiophene ring. A trend was observed in the UV-vis λ_{\max} as a function of

alkyl side chain and longer conjugation lengths in the poly(3-alkylthiophenes). Compared to the poly(3-alkylthiophenes) prepared from the oxidative polymerization, the energy absorption maximum of the regioregular polymers increase up to 14 nm in solution, and 46 nm in the solid state. The oxidation of poly(3-dodecylthiophene) with I₂ leads to polymer samples with average conductivities of 600 S cm⁻¹ and maximum conductivities of 1000 S cm⁻¹, which are 50 to 60 fold higher than the polymers synthesized by the usual chemical or electrochemical methods.⁵⁹ The McCullough method has also been used to make highly conductive head-to-tail heteroatom-functionalized polythiophenes⁶¹ and head-to-tail poly(3-alkylthiophene) copolymers,⁶² and optically active regioregular polythiophenes.⁶³

1.2 Low Bandgap Conjugated Polymers

The development of conjugated polymers with low bandgaps in their neutral state is of current interest in the field of electroactive materials because of their high intrinsic conductivities and good nonlinear optical properties.⁶⁴⁻⁷³ Though most conjugated polymers are wide-bandgap semiconductors in their neutral state, the introduction of side groups to induce specific electronic interactions with the conjugated backbone opened the way to the design of low bandgap polymers. Polythiophene, which has an intrinsic bandgap of about 2 eV, appears to be an ideal parent polymer because of the ease of substitution on the carbons in the β-position without causing strong steric interactions. The most synthesized low bandgap conjugated polymers belong to thiophene-based polymer systems.

Bredas and coworkers have shown that the bandgap is more or less proportional to the bond length alternation along the polymer backbone.⁶⁴⁻⁶⁶ The presence of both aromatic and quinoid heterocycles in the polymer will reduce a bandgap through the relaxation of bond length alternations along the polymer backbone. Another promising strategy for designing low bandgap polymers is the copolymerization of electron donor and acceptor units.⁷⁴ A strategy

for obtaining low bandgap materials which is based on using monomers with reduced aromaticity whose decreased HOMO-LUMO separations can be carried over into their polymers has also been identified.⁷⁵

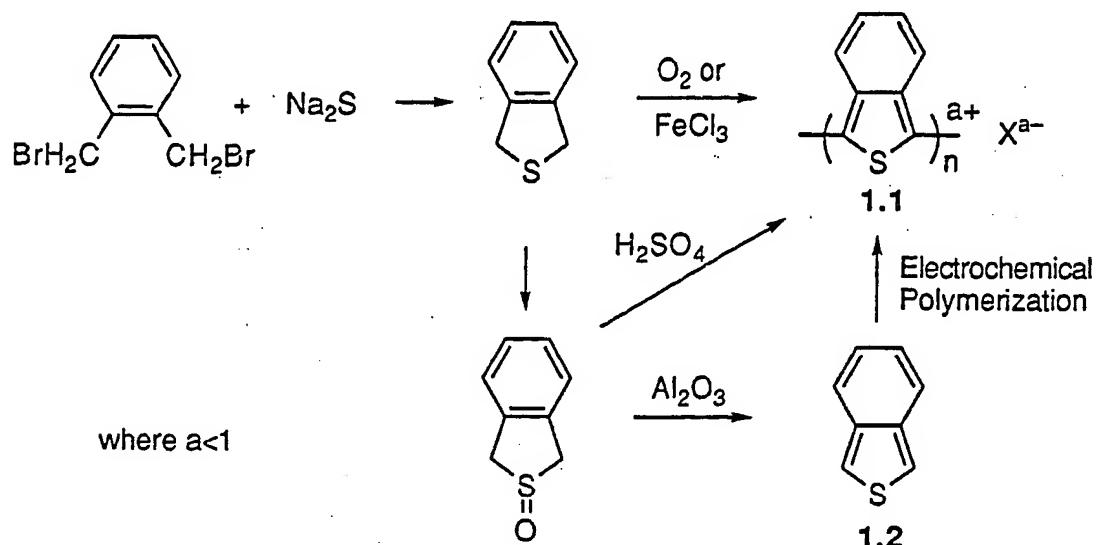
1.2.1 Poly(isothianaphthene) (1.1) and its derivatives

The first low bandgap conjugated polymer to be synthesized was poly(isothianaphthene) (1.1),⁷⁶ which has a bandgap of about 1 eV, about 1 eV lower than the bandgaps observed in polythiophene. Poly(isothianaphthene) (1.1) was prepared chemically or electrochemically from isothianaphthene (1.2)⁷⁶ which was produced by dehydration of dihydroisothianaphthene S-oxide. Addition of concentrated sulfuric acid to dihydroisothianaphthene S-oxide also resulted in the formation of the desired partially doped polymer. In 1986, Jen and Elsenbaumer⁷⁷ discovered a convenient procedure for preparing conductive poly(isothianaphthene) (1.1) directly from 1,3-dihydroisothianaphthene, eliminating two synthetic steps from the electrochemical route and one from the chemical route which was used by Wudl et al., (Scheme 1.3). The process included exposing the monomer to oxygen and/or to an oxidant such as FeCl₃ to form in one step the conductive polymer powders with conductivities as high as those previously reported. The formation of polyisothianaphthene films by oxidation of the reduced precursor polymer poly(dihydro-isothianaphthene) was reported by Rose et al.⁷⁸ Since the precursor polymer was soluble in a number of solvents, the films could be made by the precursor polymer solution and be subsequently converted to the conjugated polymer by chemical or electrochemical oxidation.

Upon doping with iodine, the electrical conductivity of poly(isothianaphthene) thin films increased to about 50 S cm⁻¹.⁷⁹ The electronic absorption spectra obtained after chemical or electrochemical doping of poly(isothianaphthene) were essentially identical. After doping, there was no indication of an energy gap over the spectral range which suggests that the electronic structure of heavily doped polymer is that of a metal.⁷⁹ The doping was

electrochemically reversible and was accompanied by a high-contrast electrochromic color change. The blue-black color of polymer thin film in the undoped state became transparent yellow upon doping. The fact that the polymer film absorbed less visible light in the doped state than in the neutral state made it the first example of a transparent highly conducting organic polymer.

Scheme 1.3



The high contrast electrochromic phenomenon associated with doping appears to be a general feature of conducting polymers.⁸⁰⁻⁸² The extent of such spectral changes depends on the initial magnitude of the polymer energy gap. If the energy gap is greater than 3 eV (absorption $\lambda < 413$ nm), the neutral insulating polymer is transparent or lightly colored, whereas after doping the conducting polymer is highly absorbing in the visible light range. However, if the energy gap is smaller than 1.5 eV ($\lambda > 620$ nm), the undoped polymer will be highly colored, whereas after doping the absorption can be relatively weak in the visible range and the absorption maximum will move to the near infrared range. Therefore, conjugated polymers with low bandgap ($E_g < 1.5$ eV) will be much less colored upon doping.

The decrease in bandgap when going from polythiophene to poly(isothianaphthene) can be explained by realizing that the fusion of a benzene ring onto the thiophene ring effectively increases the quinoid contributions to the electronic structure, which destabilizes the HOMO and stabilizes the LUMO.⁸³ The aromatic and quinoid structures of poly(isothianaphthene) are shown in Figure 1.7. Kertesz and coworkers also calculated a quinoid geometry to be the energetically favored state for poly(isothianaphthene).⁸⁴ The theoretical calculations by Marynick and coworkers suggested that the planar quinoid form was more stable than the aromatic form and the backbone of the aromatic form was twisted.⁷³ The calculated bandgaps for the quinoid form and the twisted aromatic form were 0.8 and 1.64 eV, respectively.⁷³ The ground state of poly(isothianaphthene) was assigned a quinoid structure by the Raman spectra of the neutral and doped polymers.^{67,85} The quinoid ground state geometry was also supported by NMR measurements.⁸⁶

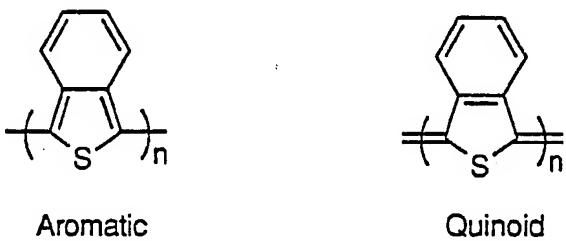


Figure 1.7. Aromatic and Quinoid structures of poly(isothianaphthene)

Using the valence effective Hamiltonian (VEH) method, Bredas et al., calculated that the bandgap of poly(isothianaphthene) is 1.17 eV lower than that of polythiophene, which is in good agreement with the experimental data.⁶⁴ Their theoretical calculations also indicated that simple dimethyl, dimethoxy, or dicyano substitutions are not expected to affect the size of the bandgap in any significant way. The VEH-calculated electronic properties of poly(5,6-dimethylisothianaphthene), poly(5,6-dimethoxyisothianaphthene) and poly(5,6-dicyanoisothianaphthene) (Figure 1.8) are almost the same as that of poly(isothianaphthene).

The effect of substitution including electron donating and electron accepting groups on the bandgaps and ionization potentials is very small.

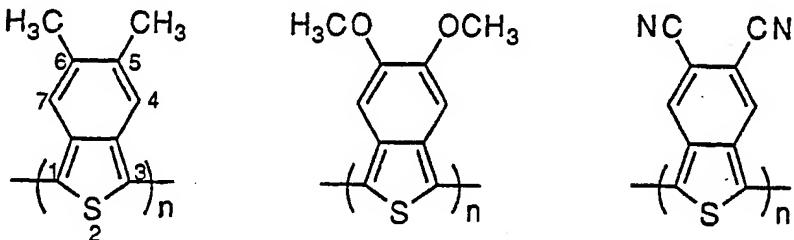
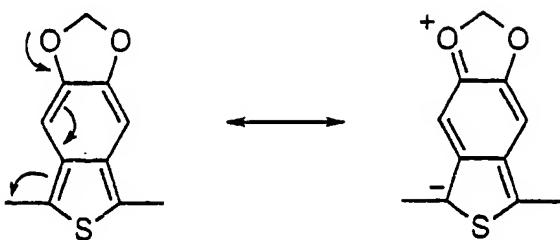


Figure 1.8. Structures of the poly(isothianaphthene) derivatives

A poly(isothianaphthene) derivative with a chemical structure where an electron-donating dioxymethylene group was introduced at the 5- and 6-positions of the isothianaphthene, poly(5,6-dioxymethyleneisothianaphthene), was synthesized in order to improve the oxidation stability of poly(isothianaphthene) (Scheme 1.4).⁸⁷ The polymer can be prepared by different polymerization routes using both electrochemical and chemical methods from the monomers 5,6-dioxymethyleneisothianaphthene and 1,3-dihydro-5,6-dioxymethyleneisothianaphthene, respectively. The introduction of an electron-donating substituent on the isothianaphthene ring was surprisingly observed not to affect the oxidation potential for polymerization. An optoelectrochemical study showed that this structural modification did not lead to significant changes in the electrochemical and optical properties of poly(isothianaphthene). The bandgap (1 eV) of the polymer thin film is comparable to that of its parent polymer, poly(isothianaphthene).

The 5- and/or 6-substituted poly(isothianaphthenes), 5-methyl-, 5-chloro-, 5-fluoro- and 5,6-dichloro-substituted poly(isothianaphthenes) have been electrochemically prepared.^{88,89} Substituents showed little effect on the redox potentials for p-doping of these substituted poly(isothianaphthenes) while substitution with electron-withdrawing groups

Scheme 1.4

considerably facilitated the n-doping.^{88,89} The bandgaps of these substituted poly(isothianaphthalenes) were similar to that of their parent polymer. Poly(tetrafluoroisothianaphthene) had a high bandgap (2.1 eV) because of increased steric hindrance.⁹⁰

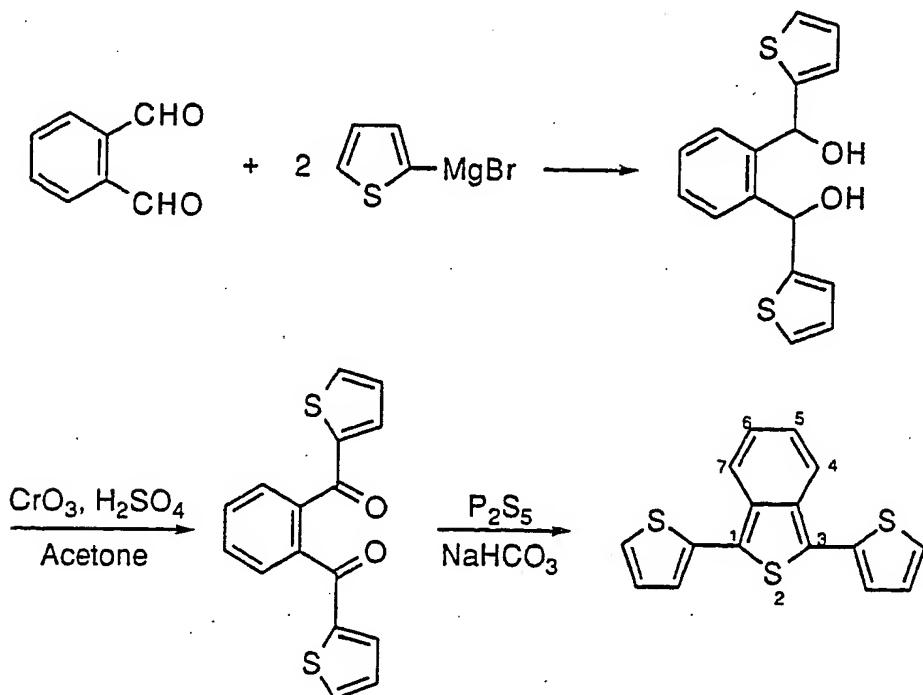
The processable poly(isothianaphthene) derivatives, poly(5-alkylisothianaphthalenes), have been prepared by FeCl_3 oxidative polymerization of 5-decyl-1,3-dihydro-isothianaphthene⁹¹ and electrochemical polymerization of 5-alkylisothianaphthene (alkyl = C_8H_{17} ; $\text{C}_{12}\text{H}_{25}$; $\text{C}_{18}\text{H}_{37}$).⁹² The poly(5-alkylisothianaphthalenes) were reported to be soluble in a number of organic solvents. The bandgap of 1.0-1.3 eV for poly(5-decyl-isothianaphthene) film and the electrical conductivity of $10^{-2} \text{ S cm}^{-1}$ for poly(5-dodecylisothianaphthene) were similar to those of the unsubstituted polymer.^{91,92} Upon doping with NOBF_4 , the CHCl_3 solution of poly(5-decylisothianaphthene) changed from the dark blue-black to a light yellow transparent solution.⁹¹

The theoretical calculations on semiconductor superlattices containing both thiophene and isothianaphthene units predict a decrease in the energy gap from the polythiophene system upon addition of isothianaphthene units.⁹³ It was also suggested that the energy gap of the copolymer should be between the bandgaps of the two homopolymers.⁹⁴ The theoretical calculations have shown that steric interactions between the sulfur and the hydrogens at the 4,7 positions in isothianaphthene dimers would drive the adjacent rings out of coplanarity.^{73,95} The copolymers that possess segments of thiophene and isothianaphthene were expected to be

very interesting since they would incorporate the steric and electronic properties of the parent homopolymers.

Ferraris et al., reported a copolymer of thiophene and isothianaphthene which was prepared from an electrochemical polymerization of 1,3-di(2'-thienyl)benzo[c]thiophene.⁹⁵ The monomer was prepared in a good yield in a three-step synthesis (Scheme 1.5). The energy gap of the polymer thin film determined from the absorption bandedge of the UV-vis-NIR spectrum was 1.7 eV, which was in agreement with the bandgap of 1.65 eV of the same polymer prepared by Cava and his coworker.⁹⁶ This experimental value agrees with compositionally adjusted linear combination of the energy gaps of the homopolymers. The two-probe dc electrical conductivity of compressed pellets of iodine doped polymer was $1.3 \times 10^{-2} \text{ S cm}^{-1}$.

Scheme 1.5

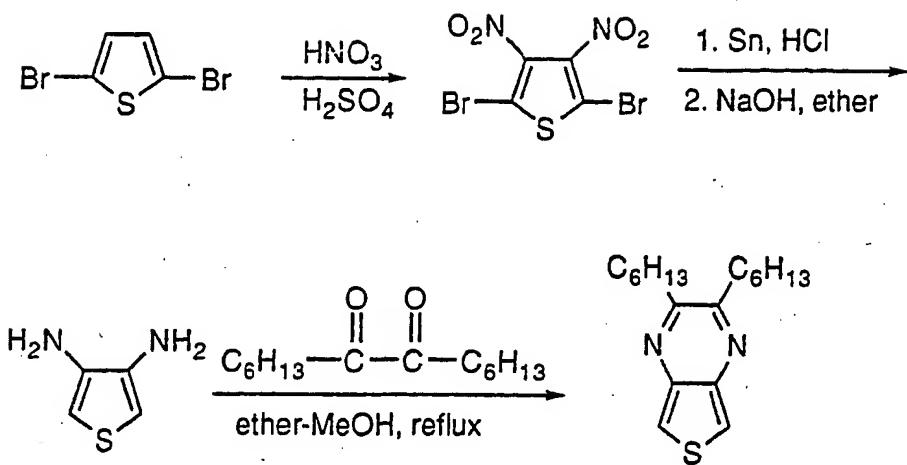


1.2.2 Poly(thieno[3,4-b]pyrazine) and its derivatives

Marynick and coworkers⁷³ have predicted that poly(isothianaphthene) has a nonplanar aromatic form because of steric interactions between the sulfur and hydrogen atoms from adjacent monomeric units and that the planar quinoid form of poly(isothianaphthene) is 2.4 kcal per unit chain length more stable than the aromatic nonplanar form. Similar calculations have also shown that poly(thieno[3,4-b]pyrazine) has planar structures in both the aromatic and the quinoid forms though the quinoid form is 4.2 kcal per unit chain length more stable than the aromatic form. The bandgaps of poly(thieno[3,4-b]pyrazine) for the quinoid and aromatic forms were calculated to be 0.70 and 0.12 eV respectively, which were lower than the calculated bandgaps of 0.80 and 1.64 eV for the quinoid form and the aromatic forms of poly(isothianaphthene).

Poly(2,3-dihexylthieno[3,4-b]pyrazine), was synthesized and studied by Pomerantz et al.^{91,97} The monomer, 2,3-dihexylthieno[3,4-b]pyrazine, was prepared in a multi-step synthesis as shown in Scheme 1.6. Polymerization was performed in CHCl₃ solution by the oxidative coupling of the monomers using FeCl₃ as an oxidant, while dry air was bubbled through the reaction mixture. In contrast to poly(isothianaphthene), this polymer is soluble in common organic solvents and thus easily processable, which makes it very attractive for applications. The UV-vis-NIR spectrum of the polymer film showed an absorption maximum at 915 nm with the bandgap (band edge) of about 0.95 eV. This bandgap value agrees quite well with the calculated bandgap (0.70 eV) of the planar quinoid form and is lower than that of poly(isothianaphthene). The polymer was dark blue-black in the neutral state and became transparent light yellow when doped with nitrosonium tetrafluoroborate. The conductivities of the doped polymer films were up to 3.6×10^{-2} S cm⁻¹.

Scheme 1.6



Recently a vibrational analysis of poly(thieno[3,4-b]pyrazine) and its derivatives by resonance Raman scattering and theoretical calculations has been reported.⁹⁸ The various derivatives substituted with alkyl side groups as long as $n\text{-C}_{13}\text{H}_{27}$ and thiophene groups have been prepared and characterized. Alkyl substitution has only a minor influence on the electronic structure of the polymer, whereas substitution with thiophene groups leads to a change of π -electron density along the polymeric backbone. From energetics calculations and from a comparison of the experimental and theoretical vibrational results, it has been shown that the polymer should have the quinoid ground-state geometry in the neutral state and aromatic in the doped state.^{98,99}

A copolymer which consists of aromatic donor (thiophene) and *o*-quinoid acceptor (thieno[3,4-b]pyrazine) units has been synthesized by Yamashita et al.¹⁰⁰ Compared with the isoelectronic copolymer of the thiophene and isothianaphthene units, the distinguishing structural feature of this system is the absence of steric repulsions between the hydrogen atom on the fused benzene ring and the sulfur atom of the adjacent thiophene (Figure 1.9).

Therefore, this copolymer is expected to have a coplanar conformation resulting in an efficient π -electron delocalization along the backbone.

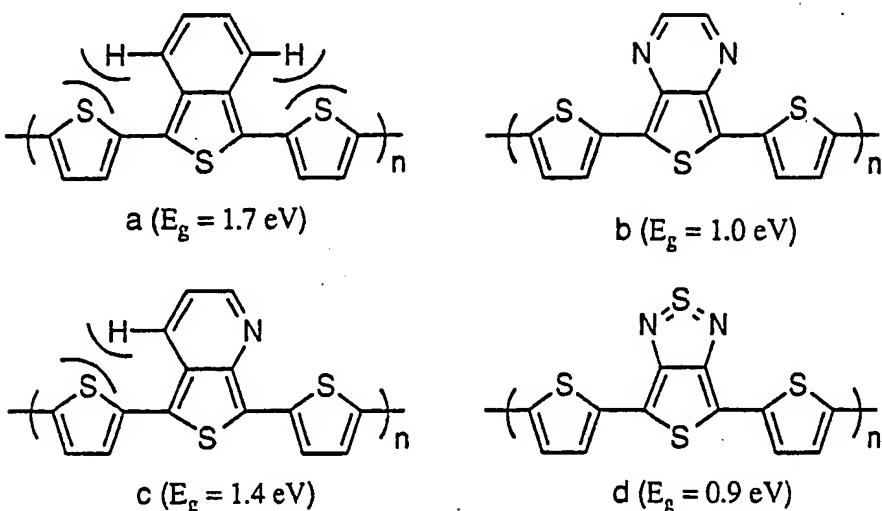


Figure 1.9. Molecular structures of the copolymers of thiophene with isothianaphthene (a), thieno[3,4-b]pyrazine (b), pyridino[2,3-c]thiophene (c) and thieno[3,4-c][1,2,5]thiadiazole (d).

The monomers, 5,7-di(2'-thienyl)thieno[3,4-b]pyrazine and its derivatives, were prepared by using a method similar to the synthetic route leading to 2,3-dihexylthieno[3,4-b]pyrazine.^{91,97} The electrochemical or chemical polymerization afforded the corresponding polymer (Fig. 1.9, b). The polymer (b) showed a bandgap of 1.0 eV, which is 0.7 eV lower than that of the related polymer (a). This fact can be attributed to the coplanarity in the polymer backbone which was suggested by the X-ray structural analysis. A similar polymer, poly(4,6-di(2'-thienyl)thieno[3,4-c][1,2,5]thiadiazole) (Fig. 1.9, d), showed a bandgap of 0.9 eV.^{72,101}

It is very interesting that a copolymer of the thiophene and pyridino[2,3-c]thiophene (Figure 1.9, c) with one steric repulsion between the hydrogen atom on the fused pyridine ring and the sulfur atom of the adjacent thiophene instead of two repulsion per repeat unit in the

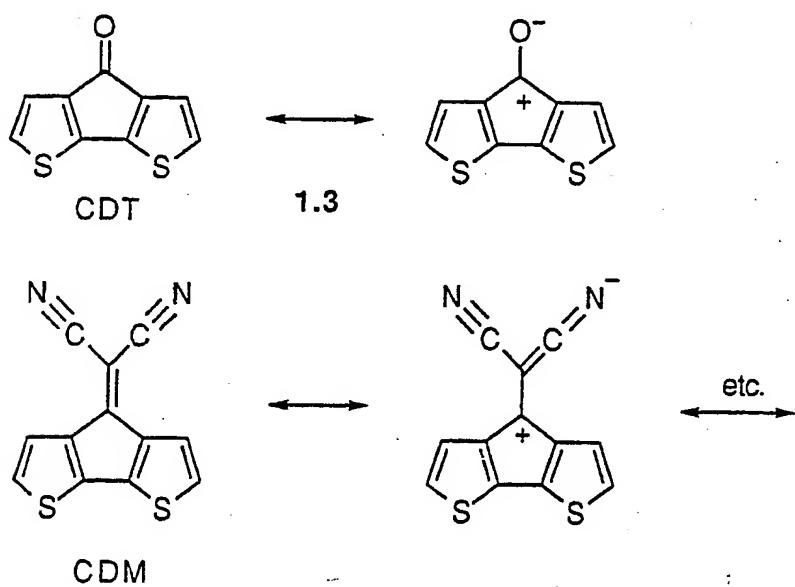
polymer (a) has a bandgap of 1.4 eV which is between the polymer (a) and the polymer (b).⁷⁰

The reduction in bandgap for the polymer (c) compared to the polymer (a) could be due to the smaller steric interaction between the thiophene and the fused pyridine ring on its nitrogen side.

1.2.3 Poly(cyclopenta[2,1-b;3,4-b']dithiophene) derivatives

In the poly(isothianaphthene) and poly(thieno[3,4-b]pyrazine) derivatives, the reduction in the bandgap was ascribed to an increased contribution of the quinoid structure. Ferraris et al., have tested another strategy for obtaining the low bandgap materials which is based on using monomers of reduced aromaticity whose decreased HOMO-LUMO separations¹⁰² can be carried over into their polymers. They selected 4H-cyclopenta[2,1-b; 3,4-b']dithiophen-4-one (CDT) (1.3) and 4-dicyanomethylene-4H-cyclopenta[2,1-b; 3,4-b']dithiophene (CDM) as the monomers, respectively.^{75,103} These two monomers should possess reduced aromaticity because of the presence of the resonance structures which push the fused ring structure toward a 12 π electron non-aromatic system (Scheme 1.7).

Scheme 1.7



The polymers, which were obtained by electrochemical polymerization, showed bandgaps of 1.2 eV for CDT and 0.8 eV from CDM. The dicyanomethylene group in CDM is a stronger electron-withdrawing substituent than the carbonyl in CDT. Therefore, the poly(4-dicyanomethylene-4H-cyclopenta[2,1-b, 3,4-b']dithiophene) (PCDM) showed the lower bandgap because of the enhanced participation of the non-aromatic resonance contributor to the overall structure of the molecule. A recent theoretical calculation showed a small bandgap (0.16 eV) of PCDM, which is mainly due to a strong stabilizing interaction occurring between the LUMO of the conjugated skeleton associated to the polymer and the LUMO of the electron-withdrawing group.¹⁰⁴ PCDM was also reported as a both p- and n-dopable polymer.¹⁰⁵

Roncali and his coworkers have demonstrated that rigidification constitutes an efficient strategy for the reduction of the HOMO-LUMO gap.¹⁰⁶⁻¹⁰⁹ They showed that polymers derived from rigidified bithienyl and terthienyl exhibit significantly smaller bandgaps than their non-rigid counterparts. The bandgaps of the polymer derived from rigidified bithienyl and terthienyl are shown in Figure 1.10. The longer π -conjugated system plays an important role in the reduction of the bandgaps.

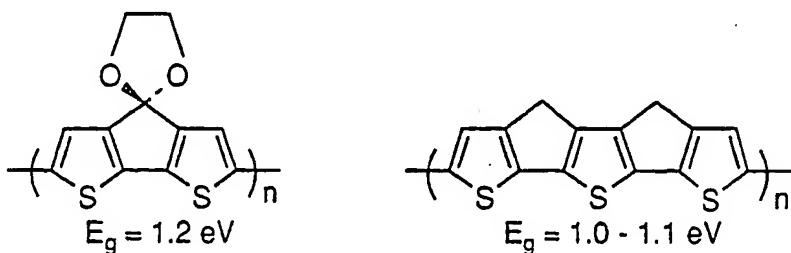


Figure 1.10. Molecular structures and bandgaps of polymers derived from rigidified bithienyl and terthienyl

1.2.4 Polymers with alternating strong donor and acceptor moieties

The concept of a regular alternation of conjugated strong donor and acceptor-like moieties in a conjugated back-bone has been used to design low bandgap conjugated

polymers.¹¹⁰ Strong donors and acceptors are needed to achieve the synthesis of very low bandgap polymers, whereas the alternating weak donor and acceptor moieties can not effectively result in low bandgap polymers.¹¹¹ The bandgap is expected to be the smallest for a combination in which the electronegativity difference between donor and acceptor is the greatest. Squaric acid (SA) and croconic acid (CA) were found to be strong acceptor moieties while strong donor-like moieties can be found in hetero ring systems with N, S or O atoms.^{74,110} The molecular structures and bandgaps of the representative low bandgap polymers are shown in Figure 1.11. The bandgap of 0.5 eV is the smallest experimental bandgap for any reported conjugated polymer. The water soluble polysquaraine (1.4, R = (CH₂)₃SO₃⁻, E_g = 1.2 eV) and polycroconaine (1.5, R = (CH₂)₃SO₃⁻, E_g = 0.7 eV) were recently reported.¹¹²

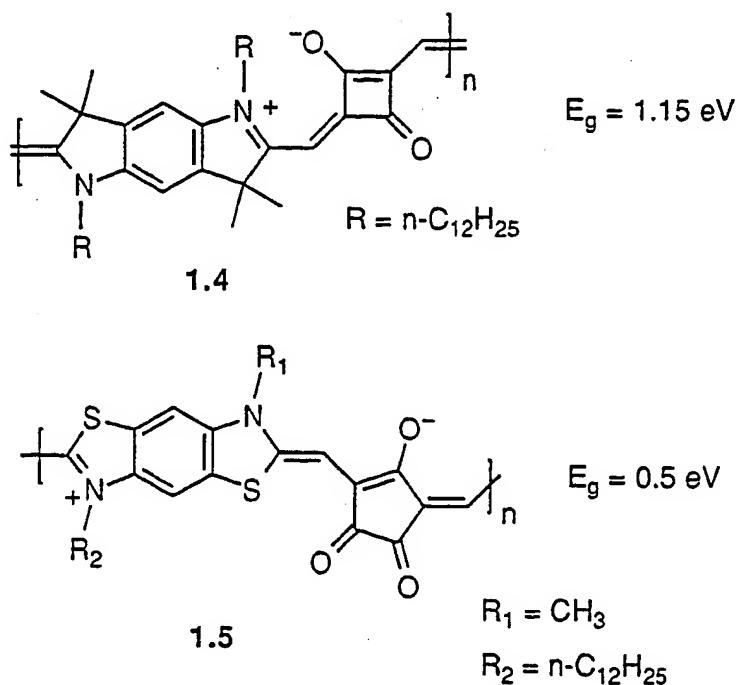
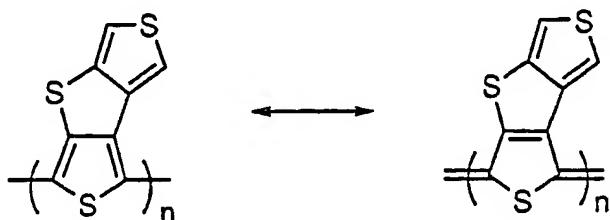


Figure 1.11. Molecular structures and bandgaps of the low bandgap polymer with alternating strong donor and acceptor moieties

1.2.5 Poly(dithieno[3,4-b;3',4'-d']thiophene)

Taliani and coworkers have prepared poly(dithieno[3,4-b;3',4'-d']thiophene) via electrochemical polymerization of dithieno[3,4-b;3',4'-d']thiophene.^{113,114} The monomer possesses four quasi-equivalent α carbon sites, which in principle may lead to the formation of a quasi-two-dimensional network of conjugated chains upon polymerization.¹¹⁵ Though in principle all the configurations that involve two, three and four bridgings between the α -positions are possible, the polymer was suggested to have the structure shown in Scheme 1.8 according to their experimental data.¹¹⁴ The bandgap of the polymer is of the order of 1.1 eV. A strong electrochromic effect between a semitransparent (conducting state) and an opaque (undoped state) form has also been observed. The electrical conductivity of the polymer film was 1.0 S cm^{-1} , compared with the $5 \times 10^{-2} \text{ S cm}^{-1}$ of the pressed pellets from photochemical polymerization of the same monomer.¹¹⁶

Scheme 1.8



Aromatic and quinoid forms of poly(dithieno[3,4-b;3',4'-d']thiophene)

1.2.6 Poly(heteroarylene methines)

Poly(heteroarylene methines) is a class of low bandgap conducting polymers which directly incorporate quinoid moieties in the conjugated polymer backbone. It was proposed

that materials with bandgap values intermediate between the quinoid and aromatic geometries would be obtained by incorporating both aromatic and quinoid isomers in the same polymer chain.¹¹⁷ A general two-step synthetic scheme involving precursor nonconjugated poly(heteroarylene methylenes) which can be subsequently oxidatively dehydrogenated to give the poly(heteroarylene methines) is usually used to prepare the polymers.¹¹⁸⁻¹²³ The molecular structures and bandgaps of some typical poly(heteroarylene methines) are shown in Figure 1.12.

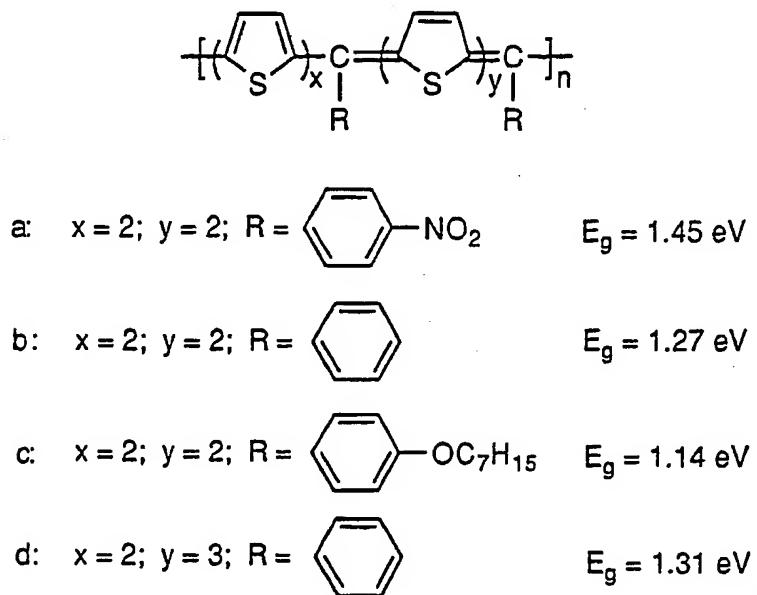


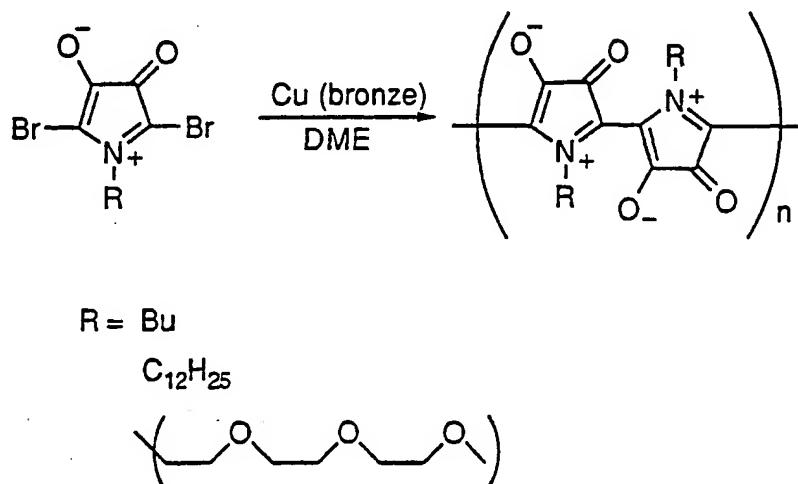
Figure 1.12. The molecular structures and bandgaps of typical poly(heteroarylene methines)

1.2.7 Zwitterionic and planar conjugated pyrrole-derived polymers

Tour and coworkers prepared unique zwitterionic pyrrole-derived polymers that can reversibly convert to a linear and planar conjugated polymer with a solution bandgap of about 1.1 eV.^{124,125} This low bandgap was the result of a structural change from the zwitterionic form to an indigo-like form which could be induced by Lewis or Bronsted bases and reversed

upon the addition of acid. Therefore, the material possesses a reversible and enormous pH-dependent or solvent-dependent spectral absorption range from the UV to the near-IR region. The polymer synthesis is shown in Scheme 1.9.

Scheme 1.9



1.2.8 Poly(3,4-ethylenedioxythiophene) and its derivatives

3,4-Ethylenedioxy substituted polythiophene, poly(3,4-ethylenedioxythiophene) (Figure 1.13 a) has been prepared chemically and electrochemically in order to increase the polymer stability.¹²⁶⁻¹²⁹ The polymer showed a low bandgap of about 1.5 eV, which was 0.5-0.7 eV lower than that of polythiophene. The incorporation of vinylene linkages between thiophene rings, making poly(bis(3,4-ethylenedioxythiophene)vinylene) (Figure 1.13 b), reduced the bandgap to 1.2 eV¹³⁰ (determined by $E_{pa, onset} - E_{nc, onset}$) or 1.4 eV¹³¹⁻¹³³ (determined by UV-vis-NIR band edge). The polymer stability was much better than that of the polythiophenes.

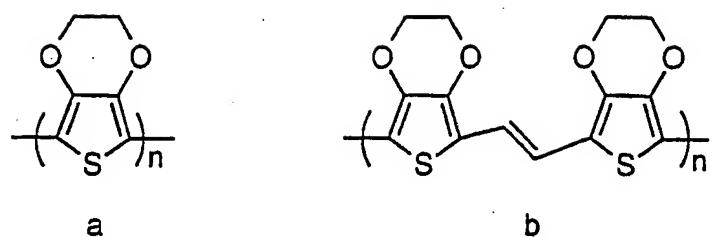


Figure 1.13. Structures of poly(3,4-ethylenedioxothiophene) (a) and poly(bis(3,4-ethylenedioxothiophene)vinylene) (b).

CHAPTER 2

SYNTHESES AND CHARACTERIZATION OF POLY(2-DECYLTHIENO[3,4-b]THIOPHENE)

Conjugated polymers with a small energy gap between occupied and unoccupied bands have attracted considerable attention in the past decade in order to develop intrinsic organic metals and new and efficient nonlinear optical materials.⁶⁴⁻⁷³ The low bandgap conjugated polymers also have potential applications as a high contrast electrochromic materials.⁷⁹ If the energy gap of the polymer is greater than 3 eV, the undoped insulating polymer is transparent (or lightly colored), whereas after doping the conducting polymer is typically highly absorbing in the visible range. However, if the energy gap is small (< 1.5 eV), the undoped polymer will be highly absorbing, whereas after doping the light absorption can be relatively weak and even transparent in the visible range. The absorption upon doping moves to the NIR range since the bandgaps of polarons and bipolarons are much lower than these of neutral polymers (see Figure 1.3 on page 5). Therefore, low bandgap polymers are normally expected to absorb less visible light in the doped conducting state than in the neutral state and provide transparent conducting materials (an exception to this phenomenon was observed by Ferraris and his coworker, the absorption in the visible range of the low bandgap polymer 1.3 (p 26) shows a slight increase in intensity upon doping⁷⁵). Since the colors can be altered via electrochemical transformations, these polymers are attractive candidates for electrochromic devices.¹⁰⁵

Our interest in electronically conducting polymers with low energy gaps has led us to prepare and study poly(2-decylthieno[3,4-b]thiophene) (2.1).^{91,97} As shown in Figure 2.1, polythiophene was chosen as a parent polymer in this system because polythiophene appears to be an ideal parent polymer due to the ease of substitution on the carbons in the β -position without causing strong steric interactions and its relatively low intrinsic bandgap of about 2 eV.

As mentioned in Chapter 1, the fusion of a benzene ring onto the thiophene ring in poly(isothianaphthene) effectively increases the quinoid contributions to the electronic structure, which destabilizes the HOMO and stabilizes the LUMO and thus reduces the bandgap.⁸³ The degree of coplanarity between adjacent repeat units and the relative amount of aromatic and quinoid character are two major determinants of the polymer energy gap.^{83,106-109} In polymer 2.1, the [3,4-b]-type fusion of a thiophene ring onto another thiophene ring should significantly increase the quinoid contribution to the electronic structure of the polymer and the energy gap would decrease relative to polythiophene. The resonance form A has quinoid character in the upper thiophene ring and aromatic character in the lower thiophene ring while resonance form B has aromatic character in the upper thiophene ring and quinoid character in the lower thiophene ring. This character of polymer 2.1 led to the prediction that resonance form A and resonance form B would have similar energy and provide a good stability to the polymer as explained as below.

Theoretical calculations⁷³ for poly(isothianaphthene) and poly(thieno[3,4-b]pyrazine) suggested that both polymers had a more stable quinoid form than an aromatic form. For poly(isothianaphthene), the planar quinoid form was 2.4 kcal per unit chain length more stable than the twisted aromatic form. For poly(thieno[3,4-b]pyrazine), the quinoid form was 4.2 kcal per unit chain length more stable than the aromatic form though both the quinoid and the aromatic forms were planar. On the other hand, the quinoid form of polymer 2.1 was predicted to have a stability comparable with that of the aromatic form and the introduction of an alkyl group onto the polymer was accompanied by a weak tendency to increase the stability of the aromatic form over the quinoid form.¹³⁴ While isothianaphthene has readily accessible pathways leading to benzene derivatives, thieno[3,4-b]thiophene is calculated to have less aromatic character than isothianaphthene. Though isothianaphthene was reported^{135,136} to have a slightly higher resonance energy than thieno[3,4-b]thiophene, isothianaphthene has a greater tendency to undergo addition reactions which form benzene derivatives, which have

much higher resonance energies than isothianaphthene due to the benzene ring. On the other hand, thieno[3,4-*b*]thiophene does not have such a high driving force since the product of the addition reactions would be thiophene derivatives which are less aromatic than the benzene products above.^{135,136} This means these reactions would be exothermic. The comparable stabilities and similar electronic properties of the quinoid and the aromatic forms could give polymer **2.1** a relatively higher stability than poly(isothianaphthene).

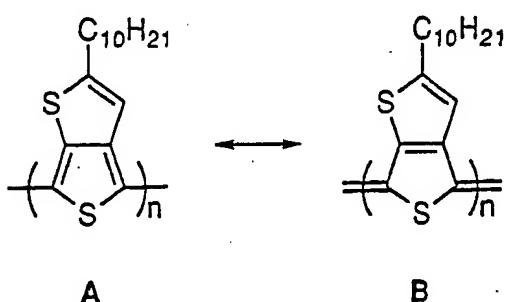


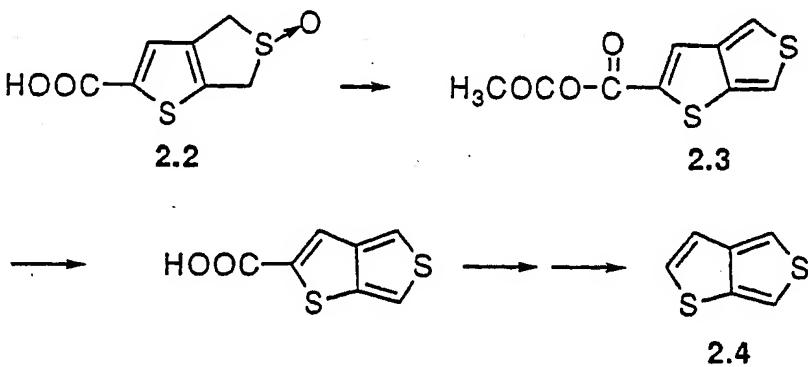
Figure 2.1 Resonance structure of poly(2-decythieno[3,4-*b*]thiophene) (2.1)

Marynick and coworkers have calculated the conformational stability and electronic structures of polymer 2.1.¹³⁴ Polymer 2.1 was expected to be a very promising conductive polymer whose aromatic and quinoid forms have comparable stabilities and similar electronic properties. Both the aromatic and quinoid forms of the polymer 2.1 were predicted to be coplanar, which is in contrast to the non-planar aromatic structure of poly(isothianaphthene) but similar to poly(thieno[3,4-*b*]pyrazine).⁹⁷ The predicted bandgap ($\pi \rightarrow \pi^*$; λ_{\max}) was 1.5~1.6 eV (775~827 nm) which is about 1 eV lower than the bandgap of polythiophene (2.6 eV (477 nm) for $\pi \rightarrow \pi^*$; λ_{\max})¹³⁴ and in about the same range as poly(isothianaphthene) (1.4 eV (886 nm) for $\pi \rightarrow \pi^*$; λ_{\max})⁷⁹ and poly(thieno[3,4-*b*]pyrazine) (1.3~1.4 eV (900~915 nm) for $\pi \rightarrow \pi^*$; λ_{\max}).

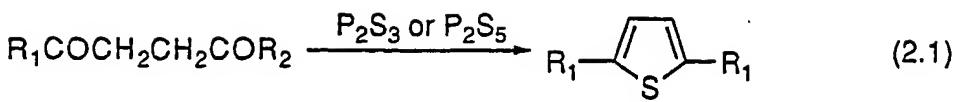
In addition, the polymer was expected to be soluble in organic solvents because a long alkyl chain was introduced on the fused ring of the polymer. Since most of the known low bandgap polymers are non-processable, this new processable low bandgap polymer would seem to be very promising.

It was reported that unsubstituted thieno[3,4-b]thiophene is very unstable at room temperature.¹³⁷ While electron withdrawing substituents increase the stability of thieno[3,4-b]thiophene, electron donating substituents decrease the stability.¹³⁷ Thieno[3,4-b]thiophene was first synthesized by Wynberg and Zwanenburg¹³⁸ using Cava's method¹³⁹ for the synthesis of benzo[c]thiophene. 4,6-Dihydro-thieno[3,4-b]thiophene-2-carboxylic acid-5-oxide (2.2) was refluxed with acetic anhydride to obtain acetic-thieno[3,4-b]thiophene-2-carboxylic anhydride (2.3) in 95% yield (Scheme 2.1). Hydrolysis of this anhydride gave the free acid in 88% yield. The decarboxylation gave thieno[3,4-b]thiophene (2.4) in 58% yield.¹³⁸ Since then many substituted thieno[3,4-b]thiophenes have been reported.¹⁴⁰⁻¹⁴²

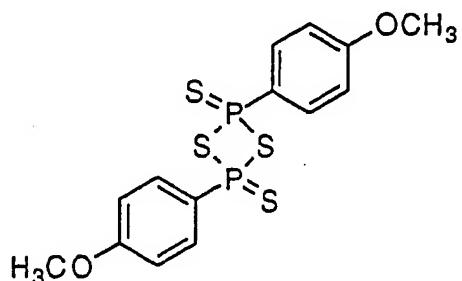
Scheme 2.1



Paal's method,¹⁴³ which involves the ring closure of 1,4-dicarbonyl compounds ($-\text{CO}-\text{CH}_2\text{CH}_2-\text{CO}-$ unit) with one of the phosphorus sulfides (equation 2.1), is a typical way to form thiophene rings. The method has been widely used to prepare a variety of thiophene-based compounds since it was first described by Paal and his coworker in 1885.¹⁴⁴

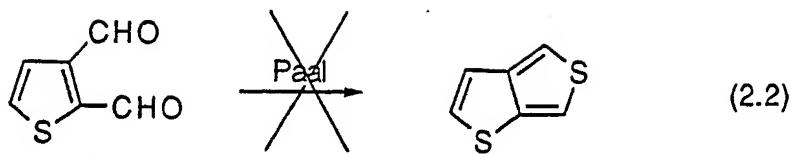


The yield of Paal's reaction is low when using P_2S_3 or P_2S_5 as a ring closing agent. An alternative to P_2S_3 or P_2S_5 is Lawesson's reagent (2.5) which has been reported to increase the yield of the reaction and reduce the side products and it can be used in mild reaction conditions.¹⁴⁵



2.5

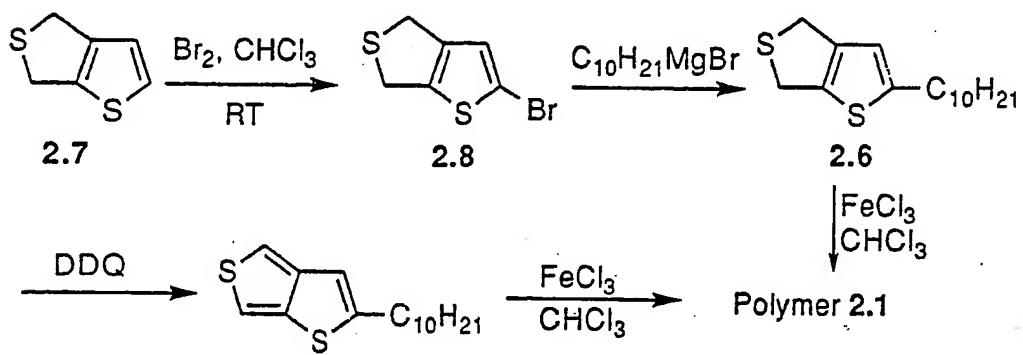
Paal's method has been widely used to make thiophene rings from 1,4-diketones and P_2S_3 or P_2S_5 . It is reasonable to consider the possibility that Paal's method might also be used in a 1,4-dialdehyde case, though no literature can be found that illustrates this kind of reaction. Unfortunately, none of the desired product was found in the reaction between 2,3-thiophenedicarboxaldehyde and the ring closing reagents (Equation 2.2). Phosphorus pentasulfide, phosphorus heptasulfide and Lawesson's reagent (2.5) were tested for use in the ring closure of 2,3-thiophenedicarboxaldehyde, but the products are all black sticky materials which do not move on TLC plates.



2.1 Route 1: via 2-decyl-4,6-dihydrothieno[3,4-b]thiophene

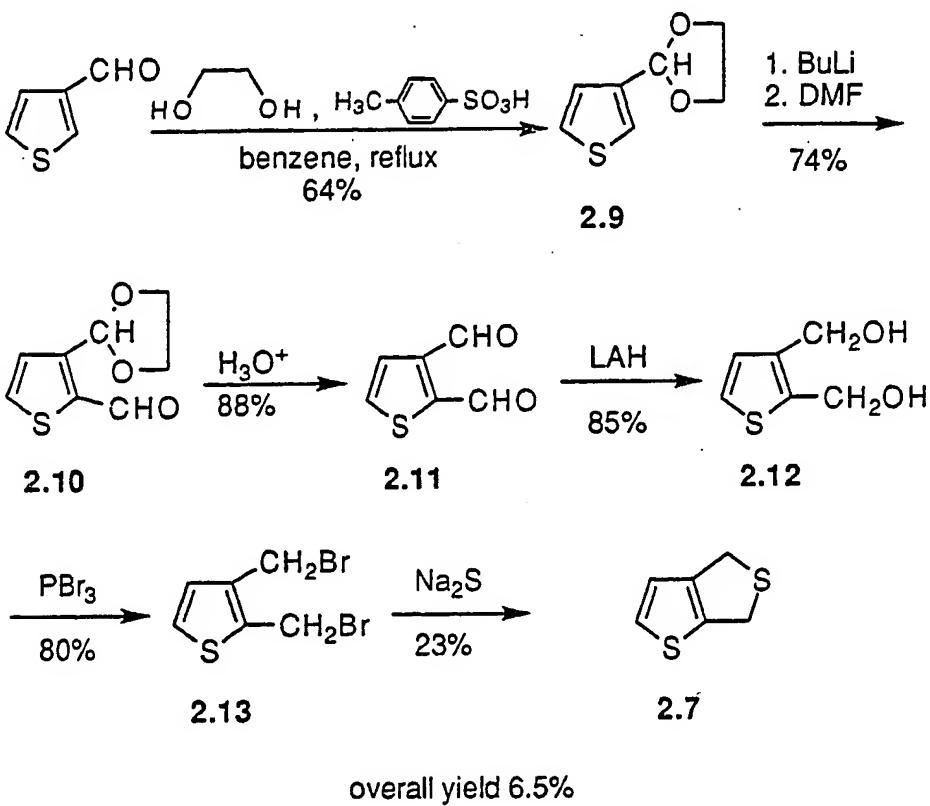
In this route, the polymer 2.1 was approached via the monomer, 2-decyl-4,6-dihydrothieno[3,4-b]thiophene (2.6) (Scheme 2.2). The synthesis of 4,6-dihydrothieno[3,4-b]thiophene (2.7) was reported in the literature.¹⁴⁶ The synthesis of 2.6 was designed so that a decyl group may be subsequently attached at 2-position of 4,6-dihydrothieno[3,4-b]thiophene (2.7). 2-Decyl-4,6-dihydrothieno[3,4-b]thiophene (2.6) may then be polymerized directly with FeCl₃ to the desired polymer 2.1 or compound 2.6 may be oxidized to 2-decylthieno[3,4-b]thiophene by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)¹⁴⁷ and then polymerized with FeCl₃ to the desired polymer 2.1.

Scheme 2.2



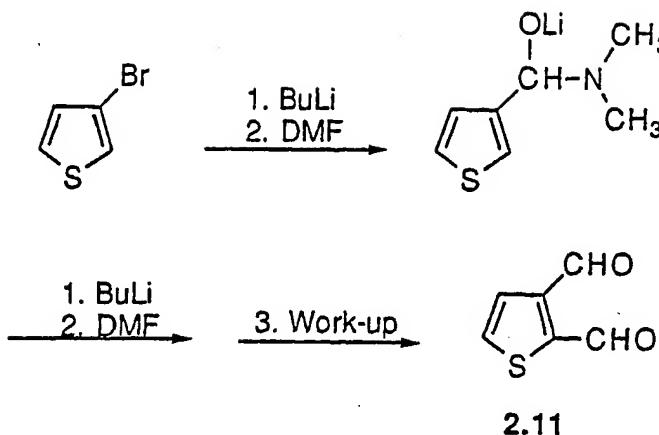
The synthetic route to 4,6-dihydrothieno[3,4-b]thiophene (2.7) is shown in Scheme 2.3, which was reported in the literature with a total yield of 6.5%.¹⁴⁶ The yields in our lab were essentially the same as reported.

Scheme 2.3



2,3-thiophenedicarbaldehyde (2.11) can also be synthesized in an one-pot reaction from 3-bromothiophene (Scheme 2.4).¹⁴⁸ The $-\text{CH}(\text{OLi})-\text{N}(\text{CH}_3)_2$ group acts as a protecting group during the addition of the second equivalent of BuLi .¹⁴⁹ This group also acts as a directing group in the second lithiation step so that the second lithium will go exclusively to the 2-position of the thiophene ring.¹⁴⁹

Scheme 2.4



2-Bromo-4,6-dihydrothieno[3,4-b]thiophene (**2.8**) was prepared by the bromination of 4,6-dihydrothieno[3,4-b]thiophene (**2.7**) with bromine in chloroform. 1.05 Equivalents of Br₂ were used in the reaction to give a yield of 45%. The orange color of bromine vanished in about five minutes. The solvent (CHCl₃) was removed under reduced pressure without work-up and the product was recrystallized from hexanes at -78 °C. The product was very unstable, and changed to black upon standing at room temperature in less than half an hour. If the reaction mixture was treated with ice in the work up process, 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (**2.8**) would decompose as indicated by the GC retention time change from 9.5 minutes for **2.8** to around 12 minutes.

Several different reaction conditions were tried for the Grignard coupling between 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (**2.8**) and 1-decylmagnesium bromide or between 4,6-dihydro-2-thieno[3,4-b]thiophenemagnesium bromide and bromodecane but none of them was found to work. NiCl₂(DPPP) was used as catalyst in all cases. 2-Bromo-4,6-dihydrothieno[3,4-b]thiophene (**2.8**) was not recovered after the reaction between **2.8** and 1-decylmagnesium bromide as shown by GC.

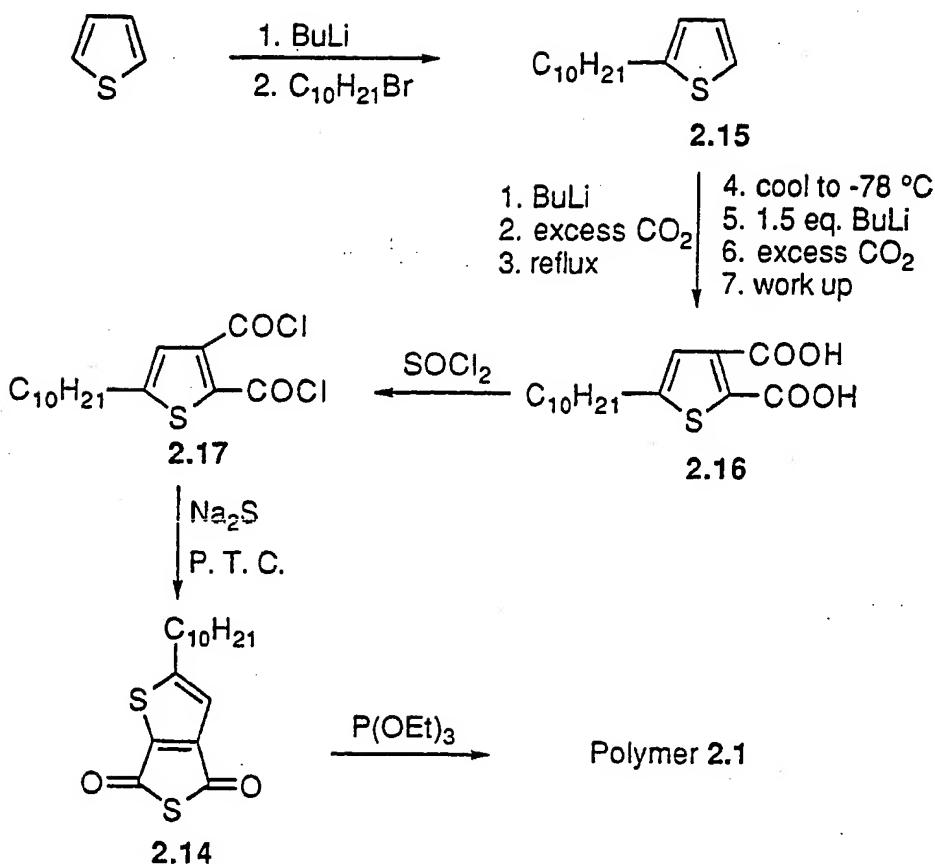
Because of the difficulty of introducing the long alkyl chain onto 4,6-dihydrothieno[3,4-b]thiophene (2.7), this synthetic route to polymer 2.1 via 2-decyl-4,6-dihydrothieno[3,4-b]thiophene (2.6) is not practical. Therefore, some other synthetic routes were designed to prepare polymer 2.1.

2.2 Route 2: via 5-decyl-2,3-thiophenedicarboxylic thioanhydride

In order to overcome the difficulty of the side chain introduction, the side chain was designed to be introduced into the molecule before the ring closure in this synthetic route. It was reported that thioanhydride molecules could be cross-coupled with each other by using $P(OEt)_3$.^{150,151} Therefore, the second synthetic route to polymer 2.1 was designed via 5-decyl-2,3-thiophenedicarboxylic thioanhydride (2.14) as the monomer (Scheme 2.5). Another advantage of this synthetic route is that it is possible to make dimer, trimer, tetramer and so on by controlling the amount of $P(OEt)_3$ used.

In this synthetic route, thiophene was selected as the starting material. 2-Decylthiophene (2.15) was made via lithiation of thiophene and coupled with bromodecane. 5-Decyl-2,3-thiophenedicarboxylic acid (2.16) was made by sequential lithiation and successive bubbling of carbon dioxide into the reaction mixture. The diacid 2.16 was then treated with thionyl chloride to yield the diacid chloride 2.17. Ring closure of the diacid chloride 2.17 with Na_2S or Li_2S gave 5-decyl-2,3-thiophenedicarboxylic thioanhydride (2.14). 5-Decyl-2,3-thiophenedicarboxylic thioanhydride was then expected to be polymerized to the polymer 2.1 by using $P(OEt)_3$ as a cross-coupling reagent (Scheme 2.5).^{150,151}

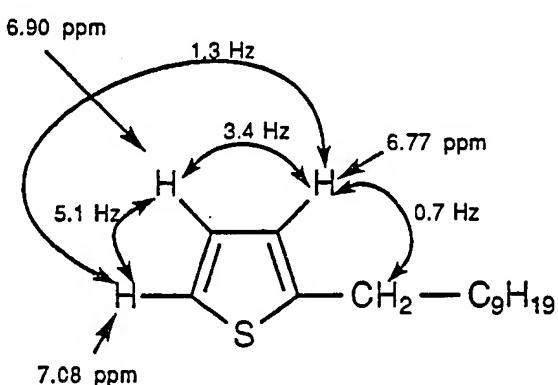
Scheme 2.5



2.2.1 Monomer synthesis

The alkylation of thiophene was done by lithiation of thiophene and then coupled with bromodecane according to a literature procedure¹⁵² which was reported for the synthesis of n-octylthiophene. The lithiation of thiophene using 1 equivalent of n-butyl lithium will generate 2-thienyllithium together with a small amount of 2,5-thienyldilithium. Upon the addition of bromodecane to 2-thienyllithium produced 2-decylthiophene (2.15). The reaction was very slow due to the low reactivity of 2-thienyllithium with bromodecane. The addition of N,N,N',N'-tetramethylethylenediamine (TMEDA) could accelerate the reaction rate from 2

days to 6 hours to complete the reaction. However, the addition of TMEDA made the reaction less clean and the product obtained had lower purity than the one without TMEDA. The total yield of 2-decylthiophene (**2.15**) was 46%. The proton NMR spectrum of **2.15** showed a coupling between the methylene protons directly attached to the ring and the 3-position proton of the ring with a coupling constant of 0.7 Hz (side chain coupling for 2-methylthiophene showed that the coupling constant of methyl protons and ring proton on 3-position is 1.10-1.15 Hz; 4-position is 0.2-0.5 Hz; 5-position is < 0.4 Hz).¹⁵³ The assignment of the ring protons of **2.15** is shown in Figure 2.2.

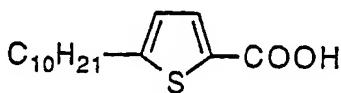


2.15

Figure 2.2. The assignment of ring ^1H NMR of compound **2.15**

There were some interesting reports^{154,155} concerning dilithiation of thiophene rings with carbonyl substituents. The carboxylate group can act to direct the metallation to an adjacent ring position if the carboxylate carbonyl group does not react with organolithium reagents such as BuLi.¹⁵⁴ The second group can be introduced onto the thiophene ring following the second lithiation at low temperature without any protection of the carboxylate group and this second group will go exclusively to the ring position adjacent to the carbonyl substituent.

5-Decyl-2,3-thiophenedicarboxylic acid (2.16) was made successfully from 2-decylthiophene with 60% yield of the desired product 2.16 and 30% yield of mono-acid product, 5-decyl-2-thiophenecarboxylic acid (2.18). No 5-decyl-2,4-thiophenedicarboxylic acid was observed in the reaction mixture. One equivalent of BuLi was used in the first lithiation reaction at room temperature and an excess of carbon dioxide was then bubbled into the reaction mixture to ensure the complete conversion of 2-decylthiophene (2.15) to lithium 5-decyl-2-thiophenecarboxylate. The reaction mixture was refluxed for one hour after the carbon dioxide bubbling in order to remove the excess carbon dioxide. The second lithiation step was run at -78 °C in order to generate the dianion and prevent the reaction between n-butyllithium and the carboxylate group of lithium 5-decyl-2-thiophenecarboxylate. 1.5 Equivalents of BuLi were used in the second lithiation step to make the dianion. Excess CO₂ was then bubbled into the reaction mixture to make 5-decyl-2,3-thiophenedicarboxylic acid (2.16).



2.18

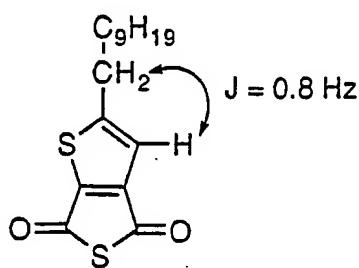
5-Decyl-2,3-thiophenedicarboxylic acid (2.16) was then treated with thionyl chloride to yield the diacid chloride 2.17. Although the diacid chloride 2.17 was hard to purify, it could be used directly in the next step of the reaction scheme. 5-Decyl-2,3-thiophenedicarboxylic thioanhydride (2.14) was made from the corresponding diacid chloride 2.17 by ring closure of the diacid chloride with Na₂S or Li₂S according to the known procedure with a slight modification.^{156,157}

The proton NMR spectrum was used to determine the structures of the isomers. The coupling constants of the methylene proton attached to the thiophene ring and the aromatic

proton were very useful for structural analysis. Table 2.1 shows the ^1H and ^{13}C NMR chemical shifts and the proton coupling constants of the ring proton and the methylene protons directly attached to the ring in the molecule 2.14.

Table 2.1. ^1H and ^{13}C NMR Spectral Data and Proton Coupling Constants of 5-Decyl-2,3-thiophenedicarboxylic Thioanhydride

	aromatic	CH_2 directly attached to the ring	$\text{C}=\text{O}$
^1H (ppm)	7.07	2.90	
Multiplicity of protons	triplet	double-triplet	
^{13}C (ppm)	163.4; 151.6; 145.5; 118.6	31.5	183.5; 180.6



2.14

A report showed that treatment of thiophthalic anhydride with diborane smoothly gave 1,3-dihydrobenzo[c]thiophene in a nearly quantitative yield.¹⁵⁸ A similar reaction of 5-decyl-2,3-thiophenedicarboxylic thioanhydride 2.14 and diborane should form 2-decyl-4,6-dihydrothieno[3,4-b]thiophene (2.3). However the treatment of 5-decyl-2,3-thiophenedicarboxylic thioanhydride with diborane did not give the desired product, and the starting material was recovered.

2.2.2 Polymer Synthesis and Characterization

Reports showed that thioanhydride molecules could be cross-coupled with each other with P(OR)₃ types of compounds.^{150,151} The monomer **2.14** could thus be polymerized by using P(OEt)₃ as a cross-coupling reagent. Advantage of this process should be that not only can the polymer be made, but by the adjusting the amount of P(OEt)₃, the oligomers could also be made. A reactant ratio of 2 : 1 of P(OEt)₃ : monomer should make the dimer; 3 : 1 of P(OEt)₃ : monomer should make the trimer; 4 : 1 of P(OEt)₃ : monomer should make the polymer.

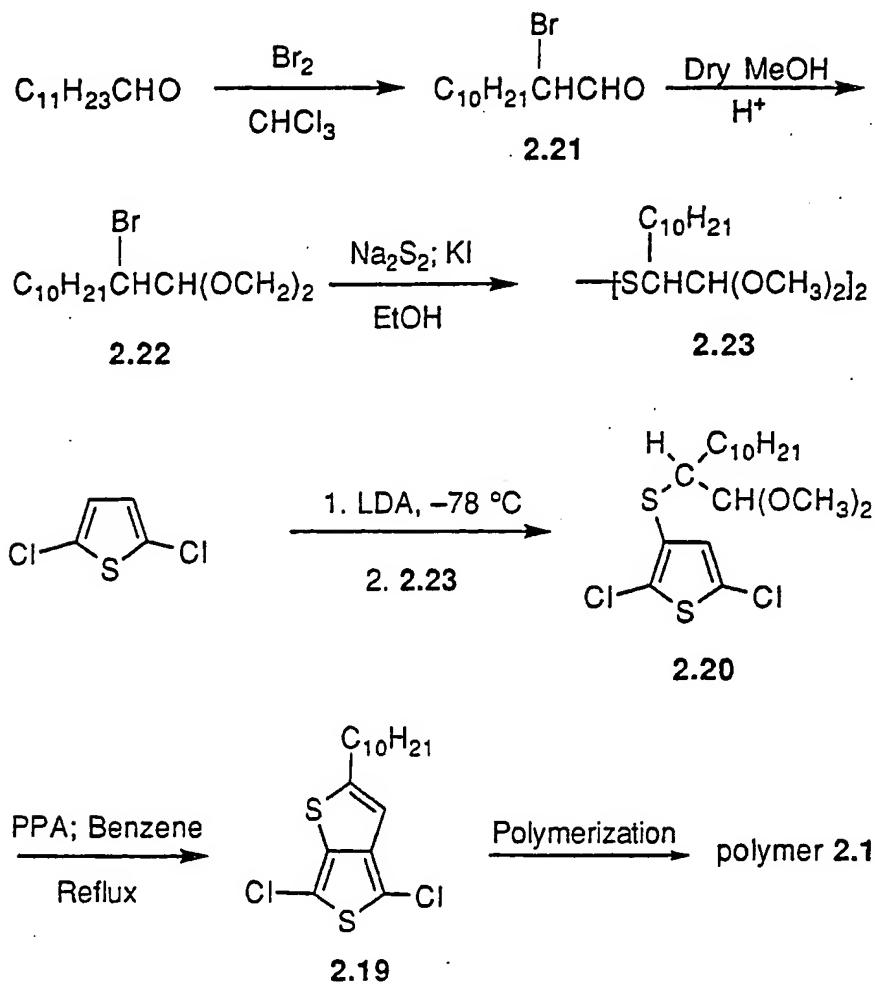
The polymerization of monomer **2.14** with P(OEt)₃ was not successful. The monomer **2.14** was refluxed under N₂ in an excess of P(OEt)₃. The extent of the reaction was monitored by TLC. The reaction was stopped after 48 hours as the TLC of the reaction mixture was no longer changing. Cooling the reaction mixture did not result in the formation of a precipitate. 10 mL of methanol was added to the reaction mixture and a precipitate formed. GPC of the precipitate showed it was a low molecular weight material, with M_n < 500. The ¹H NMR spectrum of this material showed the peaks of the long alkyl chain and two peaks at aromatic range: one was a broad peak at 7.00 ppm, the other is a sharp peak at 7.32 ppm.

2.3 Route 3: via 4,6-dichloro-2-decylthieno[3,4-b]thiophene

The polyphosphoric acid (PPA) promoted cyclization of arylthioacetaldehyde dialkyl acetals, which was first introduced by Tilak,¹⁵⁹ is one of the useful methods for preparation of thiophene rings. In this cyclization, the only prerequisite appears to be that the aryl thiols have a free ortho or peri-position to the thiol group in order to enable the cyclization of the thioglycolic aldehyde dialkyl acetal side chain. In this synthetic route (Scheme 2.6), the monomer, 4,6-dichloro-2-decylthieno[3,4-b]thiophene (**2.19**), was designed via the PPA promoted cyclization of 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (**2.20**). The

polymerization of the monomer 2.19 using a Ni(0) complex was expected to give the desired polymer 2.1.

Scheme 2.6



2.3.1 Monomer Synthesis

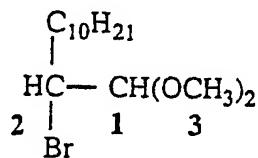
1-Dodecanal was brominated to 2-bromo-1-dodecanal (2.21) in chloroform solution. The concentration of the reaction solution must be kept dilute to get the desired product. An oxidized compound, dodecanoic acid was the main side product rather than 2,2-

dibromododecanal. When the reaction was run at higher concentration (chloroform : 1-dodecanal = 4 : 1), 90% of the reaction product was the oxidized product, dodecanoic acid. The GC retention times of 2-bromo-1-dodecanal (2.21) and dodecanic acid were coincidentally overlapped (9.5 minutes). Therefore, GC could not be used to monitor the reaction.

In order to protect the aldehyde group from attack by the LDA, 2-bromo-1-dodecanal (2.21) was refluxed in methanol to yield the dimethyl acetal, 2-bromo-1,1-dimethoxydodecane (2.22). The reaction only succeeded when the methanol was extremely dry. Even a small amount of water would drive the reaction equilibrium to the starting material side and decreased considerably the yield of the desired product. The methanol used in this reaction was distilled from Mg turnings and stored in a dry box. The ^1H NMR and ^{13}C NMR chemical shifts of 2-bromo-1,1-dimethoxydodecane (2.22) are shown in Table 2.2.

**Table 2.2. ^1H NMR and ^{13}C NMR Chemical Shifts of
2-Bromo-1,1-dimethoxydodecane**

Atom numbers	C1	C2*	C3*
^1H (ppm)	4.38	3.97	3.45
^{13}C (ppm)	106.2	55.0	55.4 and 54.9



2.22

*assignments made by continuous wave decoupling technique.

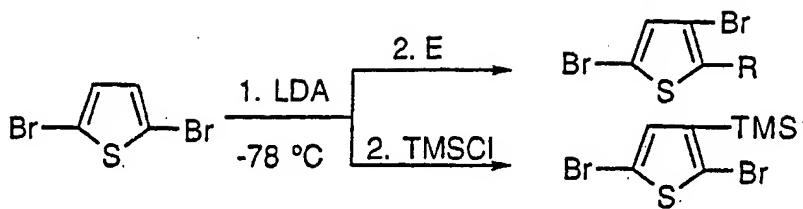
Interestingly, the two methoxy groups of 2.22 showed the same ^1H NMR chemical shift, but different ^{13}C NMR chemical shifts because of the different magnetic environment.

The carbon attached to the bromine had a very similar ^{13}C NMR chemical shift to the methoxy carbon. This made the assignment of ^{13}C NMR peaks very hard. The ^{13}C NMR peak assignments were then determined by a continuous wave decoupling technique. When the decoupler frequency for ^{13}C NMR was set at the frequency of the proton attached to carbon 2, a singlet at 55.0 ppm and two quartets centered at 55.4 and 54.9 ppm were observed. When the decoupler frequency for ^{13}C NMR was set at the frequency of the proton of the methoxy group, two singlets at 55.4 and 54.9 ppm and a doublet centered at 55.0 were observed. These experimental data indicated the chemical shifts at 55.4 and 54.9 ppm belong to the two methoxy carbons and the chemical shift at 55.0 ppm belongs to carbon 2 (the carbon attached to the bromine).

1,1-Dimethoxydodecyl-2-disulfide (2.23) was made by using a known procedure with a slight modification.¹⁶⁰ As product was hard to purify, the crude product of the disulfide was used directly in the next step reaction.

Reports showed when 2,5-dibromothiophene was treated with LDA in THF at $-78\text{ }^{\circ}\text{C}$ followed by addition of various electrophiles, the electrophiles were added at either the 2- or 3-position of the ring depending on the reactivities of the electrophiles (Scheme 2.7).^{142,161,162} When the reactivities of the electrophiles were low such as MeI, the electrophiles entered at the 2-position of the ring and the bromine migrated to the 3-position; when the reactivities of the electrophiles were high such as TMSCl, the electrophiles entered at the 3-position of the ring and the bromine stayed in the 2-position. This could be explained as follows. The reactive electrophiles reacted with the anion at lower temperature without any rearrangement, but the less reactive electrophiles reacted with the anion during the warming up of reaction mixture, after the halogen metal exchange had already happened. In the case of chlorine substituted thiophene, the chance of halogen metal exchange could be reduced very much.¹⁶³

Scheme 2.7

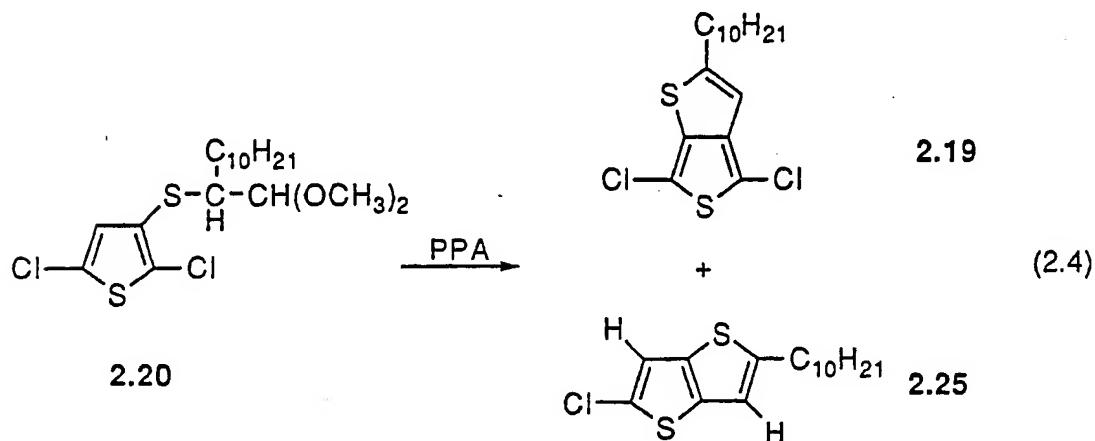
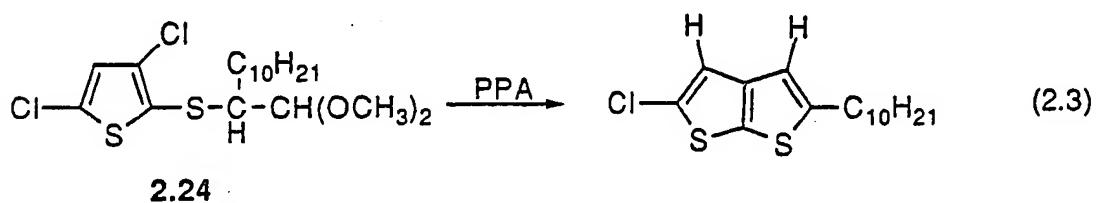


- E = MeI
 EtI
 allyl bromide
 DMF
 ethyl chloroformate
 propylene oxide
 butylene oxide
 cyclohexene oxide
 cyclohexanone
 water
 dimethyl disulfide

Based on the above facts, 2,5-dichlorothiophene was chosen as a starting material in the LDA lithiation of the 3-position of 2,5-dichlorothiophene over 2,5-dibromothiophene in order to prevent the halogen-metal migration. The reaction was carried out at $-78\text{ }^{\circ}\text{C}$ in THF. Under these reaction conditions, the chance of halogen-metal migration, leading to the undesired side product, 2,4-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.24), should be reduced very much. Half of the disulfide can be regenerated from the reaction mixture since $(\text{H}_3\text{CO})_2\text{CHCH}(\text{C}_{10}\text{H}_{21})\text{SLi}$ can be oxidized by air to the disulfide 2.23.¹⁶⁴

The ^1H and ^{13}C NMR spectrum of the product did not afford determination of whether the product was 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20) or the undesired 2,4-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.24), but this can be determined in the next step of the reaction. As shown in equations 2.3 and 2.4, only 2.24 can produce 2-chloro-5-decylthieno[2,3-b]thiophene under treatment of PPA (equation 2.3), only

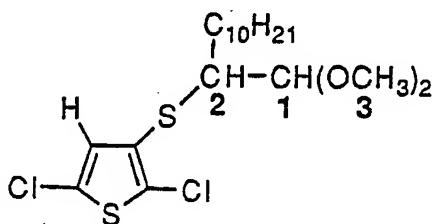
2.20 can produce 4,6-dichloro-2-decylthieno[3,4-b]thiophene (**2.19**) and 2-chloro-5-decylthieno[3,2-b]thiophene (**2.25**) (equation 2.4). From the ^1H NMR spectrum of the ring closure product, the difference should easily be distinguished. 4,6-Dichloro-2-decylthieno[3,4-b]thiophene (**2.19**) was observed in the products of the PPA ring closure. Therefore, no halogen-metal exchange had occurred during the lithiation of 2,5-dichlorothiophene and **2.20** was the major product.



The ^1H NMR and ^{13}C NMR chemical shifts of 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20) are shown in Table 2.3. The ^1H NMR showed two methoxy proton peaks, while their ^{13}C NMR chemical shifts happened to be overlapped.

Table 2.3. ^1H NMR and ^{13}C NMR Chemical Shifts of
2,5-Dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene

Chemical Shift	Aromatic	Atom 1	Atom 2	Atom 3
^1H (ppm)	6.84	4.30	3.06	3.38 & 3.42
^{13}C (ppm)	130.4, 129.1 128.7, 125.8	107.0	52.6*	55.3*



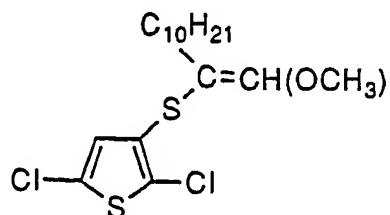
2.18

*assignments made by continuous wave decoupling technique.

Two side products were anticipated in this reaction step.¹⁶⁵⁻¹⁶⁷ They derived from the elimination of methanol from 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20) to form 2,5-dichloro-3-[2-(1-methoxydodecyl)thio]thiophene (2.26) and the corresponding aldehyde, 2,5-dichloro-3-[[(1-formylundecyl)thio]thiophene. Compound 2.26 was isolated successfully but no deprotected product, 2,5-dichloro-3-[(1-formylundecyl)thio]thiophene, was observed in the product. The ^1H and ^{13}C NMR spectra of 2.26 are shown in Table 2.4. It is not clear that this product has either *E* or *Z* alkene structure from the NMR spectra, but it is most likely has a *E* structure.¹⁶⁵ This product 2.26 can also be used in the next reaction step to get the same ring closure product.

**Table 2.4. ^1H NMR and ^{13}C NMR Spectral Data of
2,5-Dichloro-3-[2-(1-methoxydodecyl)thio]thiophene**

Chemical Shift	Aromatic(s) & alkene(s)	OCH ₃
^1H (ppm)	6.64 & 6.54	3.69
^{13}C (ppm)	152.9; 131.2; 127.6; 126.0; 122.8; 110.8	60.2

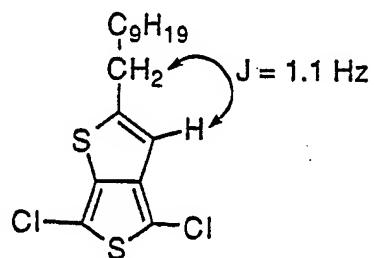


2.26

The ring closure of 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene 2.20 with PPA gave mainly a mixture of two products. One product had one aromatic proton, and the other product had two aromatic protons. They were identified as 4,6-dichloro-2-decylthieno[3,4-b]thiophene (2.19) and 2-chloro-5-decylthieno[3,2-b]thiophene (2.25) based on the following analyses. With careful adjustment of the NMR parameters, the product with one aromatic proton showed a coupling between the aromatic proton and the CH₂ attached to the thienothiophene ring. The coupling constant was 1.1 Hz. The ^{13}C NMR spectra of this product showed six aromatic carbons. The NMR spectra of this product indicated that it is 4,6-dichloro-2-decylthieno[3,4-b]thiophene (Table 2.5). The elemental analysis supported the structure of 2.19.

**Table 2.5. ^1H NMR and ^{13}C NMR Spectral Data of
4,6-Dichloro-2-decylthieno[3,4-b]thiophene**

Chemical Shift	Aromatic	CH_2 directly attached to the ring
^1H (ppm)	6.46	2.71
Multiplicity of ^1H	triplet	double-triplet
^{13}C (ppm)	154.7; 143.7; 135.8 112.4; 111.5; 110.5	31.9

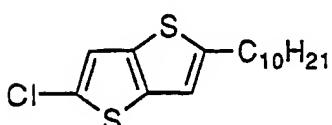


2.19

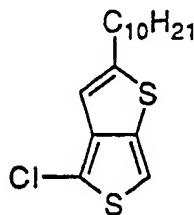
The other product in the ring closure step has a molecular formula of $\text{C}_{16}\text{H}_{23}\text{S}_2\text{Cl}$ calculated from the elemental analysis. The ^1H NMR and the ^{13}C NMR spectral data of this side product are shown in Table 2.6. The NMR data suggested three possible structures 2.25, 2.27, and 2.28.

Table 2.6. ^1H NMR and ^{13}C NMR Spectral Data of Side Product from Ring Closure

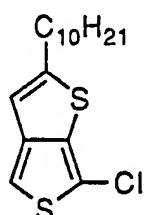
Chemical Shift	Aromatics	CH_2 directly attached to the ring
^1H (ppm)	7.05; 6.83	2.84
Multiplicity of ^1H	d; m	dt
Coupling Constants (Hz)	0.6	0.8; 7.5
^{13}C (ppm)	147.7; 136.0; 134.8; 129.0; 118.8; 116.0	31.9



2.25



2.27



2.28

In order to determine the structure of the side product, one equivalent of butyllithium was used to treat this side product and the reaction was quenched with water. As expected, the product 2.29 so generated had three aromatic protons. Two of the aromatic protons were coupled with each other (Figure 2.3) with a coupling constant of 5.3 Hz, which is a typical $J_{2,3}$ for unsubstituted thieno[2,3-b]thiophenes.¹⁵³ This compound also showed a double-triplet at 2.86 ppm and this proton was coupled with one of the aromatic protons. Therefore, this product had the structure of compound 2.29, and the ring closure side product from the earlier reaction had the structure of 2.25.

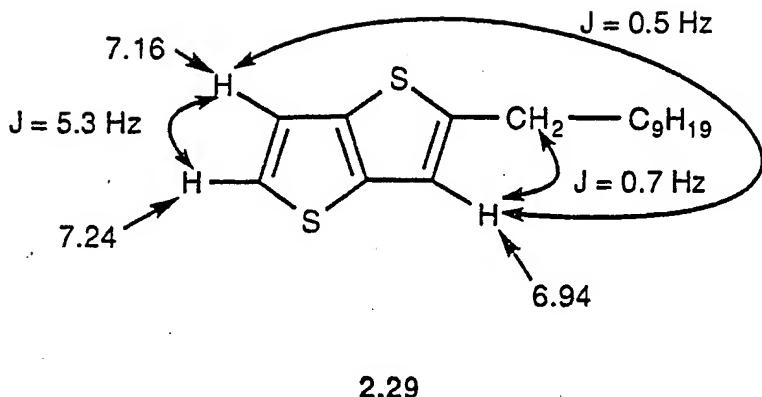


Figure 2.3. The assignment of ring ^1H NMR of compound 2.29

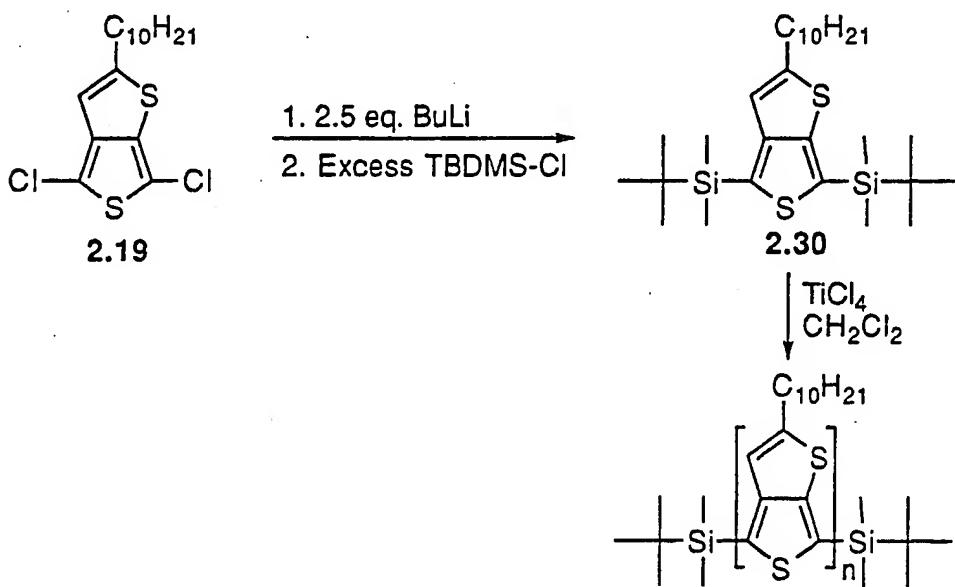
2.3.2 Polymer Synthesis and Characterization

At first, the polymerization involving the nickel-catalyzed coupling of the mono-Grignard reagent was tried for the polymerization of 4,6-dichloro-2-decylthieno[3,4-b]thiophene **2.19**. The monomer **2.19** was treated with Mg in THF but no reaction between the Mg and the monomer was observed. Mg turnings were stirred under N_2 overnight in an effort to generate fresh Mg and then the monomer was dropped in, but there was no observable reaction. The reaction also could not be initiated by 1,2-dibromoethane.

The Grignard reagent was produced when MgBr_2 was used to initiate the reaction. The formation of the Grignard reagent was confirmed by the quenching analysis. Upon quenching the Grignard reagent with water, the product was either 4-chloro-2-decylthieno[3,4-b]thiophene (**2.27**) or 6-chloro-2-decylthieno[3,4-b]thiophene (**2.28**). The ^1H NMR spectrum of the product has two aromatic protons and their chemical shifts are 6.91 ppm and 6.53 ppm. Unfortunately, this Grignard reagent could not be coupled with itself in the presence of $\text{NiCl}_2(\text{dppp})$ as a catalyst to produce the corresponding polymer. **2.27** and **2.28** were two major products after work up.

The second method of polymerization that was tried involved changing the monomer **2.19** to 4,6-bis(*tert*-butyldimethylsilyl)-2-decylthieno[3,4-b]thiophene (**2.30**) (Scheme 2.8), which might then be polymerized to the desired polymer **2.1** by using titanium chloride.¹⁶⁸ The attempt at making 4,6-bis(*tert*-butyldimethylsilyl)-2-decylthieno[3,4-b]thiophene (**2.30**) was not successful since the product turned out to be either 4-*tert*-butyldimethylsilyl-6-chloro-2-decylthieno[3,4-b]thiophene (**2.31**) or 6-*tert*-butyldimethylsilyl-4-chloro-2-decylthieno[3,4-b]thiophene (**2.32**) as calculated from elemental analysis. The reason was that the low reactivity of the dichloro compound **2.19** made it difficult for this compound to be dilithiated with BuLi. The elemental analysis confirmed that the product has the molecular formula of C₂₂H₃₇S₂SiCl.

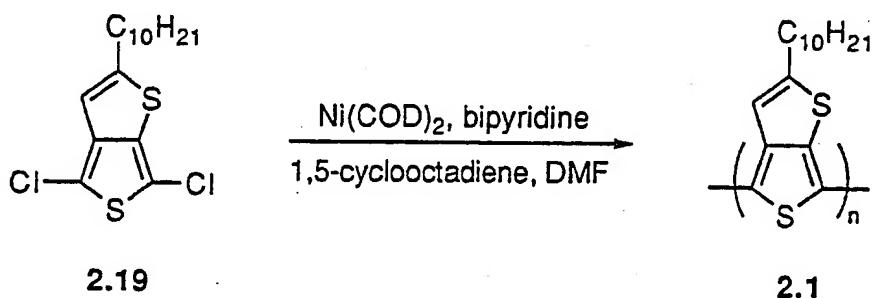
Scheme 2.8



The polymerization of monomer **2.19** was successful with Ni(0) complex (Ni(COD)₂, bipyridine, 1,5-cyclooctadiene in DMF) (Scheme 2.9). The polymer was a blue-black solid and was only slightly soluble in chloroform and THF. The GPC of the CHCl₃ soluble part of

the polymer showed a M_n of 7200 g mol⁻¹. The low solubility of this polymer may be due to very high molecular weight of the polymer formed in the Ni(0) polymerization. The same phenomena was also observed by Miyazaki et al., in the polymerization of 3-dodecyl-2,5-diiodothiophene.³¹ When 3-alkyl-2,5-diiodothiophene was polymerized with Ni(0) complex, the solubility of the resulting polymer decreased with the increase of the alkyl chain length.³¹

Scheme 2.9



Attempts to cast a polymer film were not successful due to the low concentration of the polymer solution. The UV-vis-NIR spectrum of the soluble portion of the polymer (CHCl_3 solution) showed a λ_{max} of 614 nm.

The IR spectrum of the polymer showed several absorptions just below 3000 cm^{-1} which indicated that the polymer had a long alkyl chain. The IR spectrum also showed a small aromatic proton-carbon stretch band above 3000 cm^{-1} which indicated the presence of the aromatic proton. No significant peak was found around 1100 cm^{-1} (C-Cl stretch). This is in agreement with the elemental analysis of the polymer which showed 0 % chlorine content.

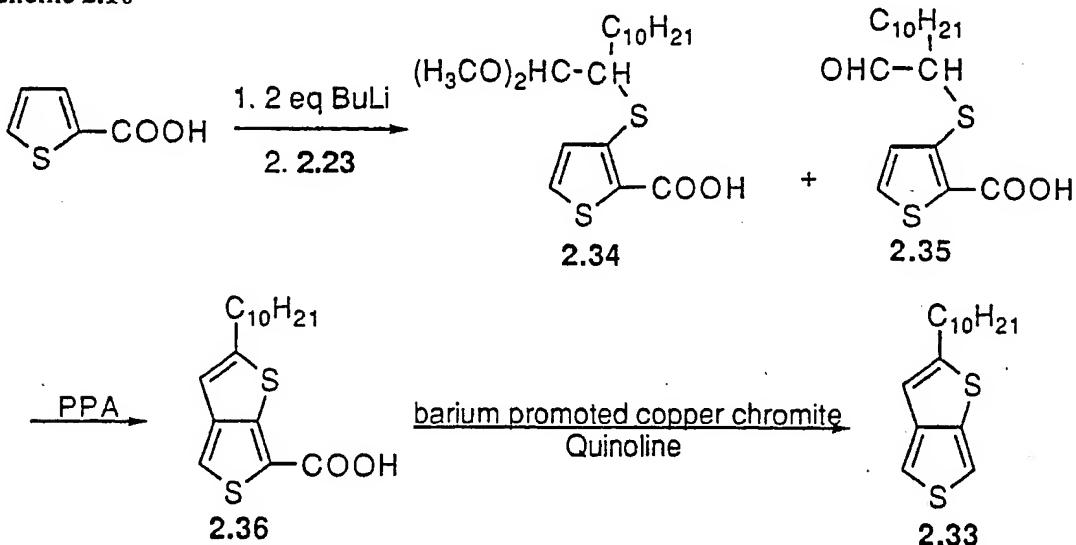
Thermogravimetric analysis was run on the polymer under N₂ with a heating rate of 10 °C min⁻¹. The polymer showed an onset of decomposition at 180 °C with 25% weight loss at 350 °C, 50% weight loss at 400 °C, and 70% weight loss at 500 °C.

The electrical conductivity of the polymer as pressed pellets was $1.4 \times 10^{-6} \text{ S cm}^{-1}$ before doping and $2.9 \times 10^{-6} \text{ S cm}^{-1}$ when doped with NOBF_4 . No significant change in the conductivity was observed for FeCl_3 doping.

2.4 Route 4: via 2-decylthieno[3,4-b]thiophene

In this synthetic route (Scheme 2.9), monomer 2-decylthieno[3,4-b]thiophene (2.33) was designed to obtain via decarboxylation of 2-decyl-6-thieno[3,4-b]thiophenecarboxylic acid (2.36) which could be obtained by the PPA promoted ring closure reaction of 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34). The COOH group was used to block the 2-position of the thiophene ring of 2.34 in the process of ring closure. As a result the ring closure site would be on the 4-position of the thiophene ring instead of the 2-position. The COOH group could then be taken off by decarboxylation with barium promoted copper chromite. 2.33 could then easily be polymerized via the traditional FeCl_3 chemical oxidative polymerization method.

Scheme 2.10

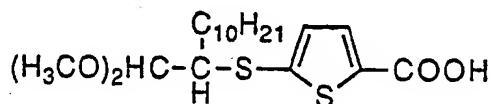


2.4.1 Monomer Synthesis

It was reported that the carboxylate group can act as a directing group during lithiation of thiophene.¹⁵⁴ When 2-thiophenecarboxylic acid was treated with 2 equivalents of butyllithium at low temperature (-78 °C), a dianion species was formed and the 3-position of thiophene ring was deprotonated rather than the 5-position. An electrophile could then be introduced onto 3-position of the thiophene ring.

After the starting material 2-thiophenecarboxylic acid was treated with 2 equivalents of butyllithium, 1,1-dimethoxydodecyl-2-disulfide (2.23) was added to yield the product, 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34). The ¹H NMR and ¹³C NMR data of compound 2.34 are shown in Table 2.7.

In order to assure that the product had the 2,3-substituted structure (2.34) rather than 2,5-substituted structure (2.37), the aromatic proton coupling constant was examined (Table 2.7). The product had a proton coupling constant of 5.2 Hz between the two aromatic protons which was the normal range of coupling constants for 2,3-disubstituted thiophenes.¹⁵³ Therefore, the product was a 2,3-disubstituted thiophene, having structure 2.34.

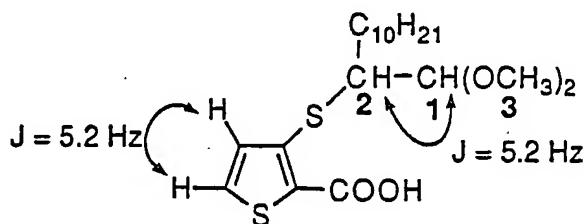


2.37

There was more than one product in the reaction leading to 2.34. A main side product was the deprotected product of 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34), which was the corresponding aldehyde, 3-[(1-formylundecyl)thio]-2-thiophenecarboxylic acid (2.35). Unlike 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20), 2.34 was very easily deprotected to form the

**Table 2.7. ^1H NMR and ^{13}C NMR Spectral Data of
3-[2-(1,1-Dimethoxydodecyl)thio]-2-thiophenecarboxylic Acid**

Chemical Shift	Aromatics	Atom 1	Atom 2	Atom 3	Acid
^1H (ppm)	7.13 & 7.56	4.35	3.30	3.41 3.44	10.88
Multiplicity of ^1H	d & d	d	m	s & s	broad
^{13}C (ppm)	143.5; 132.0; 129.2; 124.8	107.4	56.4* 55.8*	51.6*	166.3



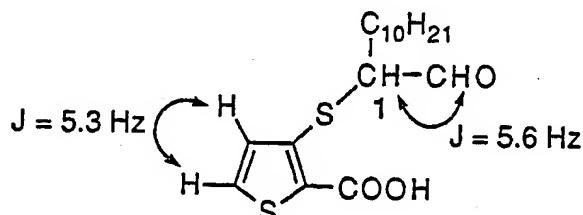
2.34

*assignments made by proton off-resonance decoupling technique.

corresponding aldehyde. The reason might be that 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid itself had an acid group which acted as an acidic catalyst so 2.34 was easily deprotected in the work up process. Fortunately, both 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34) and the corresponding aldehyde 2.35 underwent the ring closure with PPA and produced the same desired product. ^1H NMR and ^{13}C NMR data of 2.35 are shown in Table 2.8. Elemental analysis supported the structure.

Table 2.8. ^1H NMR and ^{13}C NMR Spectral Data of
3-[(1-Formylundecyl)thio]-2-thiophenecarboxylic Acid

Chemical Shift	Aromatic	Aldehyde	Atom 1	Acidic
^1H (ppm)	7.08 & 7.58	9.27	3.77	10.27
multiplicity	double	double	multiple	s
^{13}C (ppm)	142.2; 133.1 127.4; 123.1	196.1	54.6	167.1

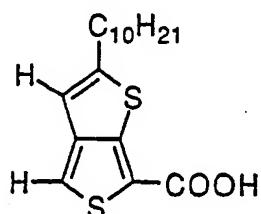


2.35

The ring closure of 2.34 and 2.35 gave 43% yield of the desired compound, 2-decyl-6-thieno[3,4-b]thiophenecarboxylic acid (2.36) and 29% yield of undesired product, 2-decylthieno[3,2-b]thiophene (2.29). The COOH group of the compound 2.34 and 2.35 did have the block effect during the ring closure reaction. The ^1H NMR and ^{13}C NMR data of 2.36 are shown in Table 2.9.

**Table 2.9. ^1H NMR and ^{13}C NMR Spectral Data of
2-Decyl-6-thieno[3,4-b]thiophenecarboxylic Acid**

Chemical Shift	Aromatic	Acid
^1H (ppm)	7.49; 6.86	10.0 (broad)
^{13}C (ppm)	113.2; 116.4; 119.8; 147.4; 147.8; 154.8	167.8



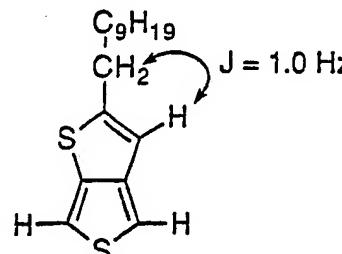
2.36

The ring closure of the 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34) also involved a major side product. The ^1H and ^{13}C NMR spectra of the side product showed that this molecule had the same ^1H and ^{13}C chemical shifts as the molecule obtained from the BuLi treatment of 2.25. This indicates that this side product has a structure of 2-decylthieno[3,2-b]thiophene (2.29).

Decarboxylation of 2-decyl-6-thieno[3,4-b]thiophenecarboxylic acid 2.36 was done according to Pei et al.'s procedure¹²⁸ with barium promoted copper chromite as a catalyst and a yield of 89%. Table 2.10 shows the ^1H NMR and ^{13}C NMR data of compound 2.33. As shown in the Table 2.10, chemical shifts of the protons at 4- and 6-positions happen to be overlapped.

**Table 2.10. ^1H NMR and ^{13}C NMR Spectral Data of
2-Decylthieno[3,4-b]thiophene**

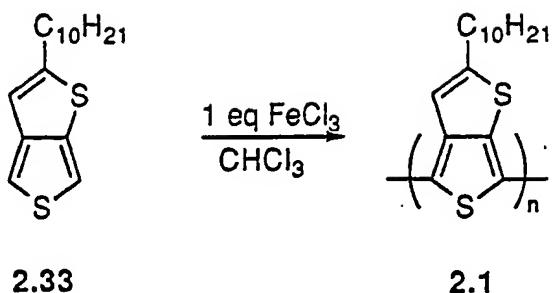
Chemical Shift	Aromatic	CH_2 directly attached to the ring
^1H (ppm)	7.13 (2H); 6.61 (1H)	2.75
multiplicity of protons	triplet	double-triplet
^{13}C (ppm)	152.9; 147.5; 138.7; 113.1; 110.1; 109.9	31.9


 2.33

2.4.2 Polymer Synthesis and Characterization

The polymerization of thiophene-based monomers with FeCl_3 is a typical oxidative polymerization method for polythiophene and its derivatives. The polymerization of monomer 2.33 was successful when one equivalent of FeCl_3 was used in the polymerization process (Scheme 2.11). The polymer was soluble in all organic solvents examined, such as CHCl_3 , THF, chlorobenzene. When four equivalent of FeCl_3 was used in the polymerization process,^{22,169} the resulting polymer was insoluble in any tried organic solvents such as CHCl_3 , THF, chlorobenzene, dichlorobenzene, DMF, or DMSO.

Scheme 2.11



Polymer synthesized with one equivalent of FeCl_3 was bluish-green in color before dedoping and the color changed to greenish-yellow upon dedoping with hydrazine. The ^1H NMR spectrum showed a small peak in the aromatic region at 6.64 ppm and non-aromatic peaks for the side chain.

The polymer films of poly(2-decylthieno[3,4-b]thiophene) was formed by casting the CHCl_3 solution on a piece of glass. The electrical conductivity of the films were $2.2 \times 10^{-5} \text{ S cm}^{-1}$ without doping, $8.8 \times 10^{-3} \text{ S cm}^{-1}$ after doping with I_2 and $7.2 \times 10^{-2} \text{ S cm}^{-1}$ after doping with FeCl_3 in CH_3OH . The electrical conductivity was measured using the standard four-in-line probe method.^{2,170} The polymer films were exposed to iodine vapor at room temperature for 24 hours. Methanol was used as the FeCl_3 doping solvent because the polymer film was soluble in nitromethane.

The UV-vis-NIR spectrum of the polymer solution (CHCl_3) showed a λ_{max} of 704 nm for dedoped polymer solution (CHCl_3) and two λ_{max} , 795 nm and 1350 nm for the doped polymer solution (CHCl_3 , doped with FeCl_3). The polymer film cast from CHCl_3 solution had a λ_{max} of 738 nm without doping. Upon doping with 0.1% FeCl_3 solution, the peak at 738 nm decreased gradually while a new peak at $\lambda_{\text{max}} = 1052 \text{ nm}$ was formed. When the polymer film was doped for 30 minutes, the peak at 738 nm disappeared. The doping was

reversible and NH₃ gas could be used to dedope the polymer films. The bandgap calculated from bandedge was 1.2 eV, (1.68 eV from λ_{max}), which is about 0.8-1.0 eV lower than the bandgap of polythiophene (2.0-2.2 eV). The bandgap (1.68 eV) calculated from the absorption maximum was very close to the bandgap (1.5-1.6 eV) from the theoretical calculation.¹³⁴

Gel permeation chromatography (GPC), using polystyrene standards, showed that the polymer had $M_n = 3.0 \times 10^4 \text{ g mol}^{-1}$ and $M_w = 4.3 \times 10^4 \text{ g mol}^{-1}$ with a polydispersity of 1.4. The GPC also had two small peaks at very high molecular range ($>10^6 \text{ g mol}^{-1}$), which could belong to aggregation of the polymer, and there were also some peaks due to oligomers.

2.5 Conclusion

Of the four synthetic routes to poly(2-decylthieno[3,4-b]thiophene) (2.1), route 1 and route 2 were unsuccessful. In synthetic route 1, the difficulty of introducing the long alkyl chain onto 4,6-dihydrothieno[3,4-b]thiophene (2.7) caused us to abandon this synthetic route via 2-decyl-4,6-dihydrothieno[3,4-b]thiophene (2.6). Kumada and his coworkers reported unsuccessful coupling between 2-bromothiophene and 1-butylmagnesium bromide.¹⁷¹ The reason may be attributed to rapid metal-halogen exchange reaction between 2-bromothiophene and 1-butylmagnesium bromide. The resulting 2-thiophenemagnesium bromide then quickly forms Ar-Mg-Ar which inhibits cross-coupling.¹⁷² In synthetic route 2, the monomer, 5-decyl-2,3-thiophenedicarboxylic thioanhydride (2.14), was successfully prepared. Although the monomer was readily prepared in three steps which was a major reason for us to design this synthetic route, the polymerization of 2.14 with P(OEt)₃ only gave low molecular weight materials. This may indicate that P(OEt)₃ coupling of thiophthalic anhydride as described in the literature¹⁵⁰ for preparing the dimer can not practically be used to prepare polymer 2.1.

The P(OEt)₃ coupling was also tried by Mullen and his coworkers to prepare polymers but no high molecular weight polymers were prepared except for some dimers and oligomers.^{173,174}

Poly(2-decylthieno[3,4-b]thiophene) (**2.1**), a low bandgap conducting polymer, was successfully synthesized by synthetic route 3 and synthetic route 4. Polymerization via 4,6-dichloro-2-decylthieno[3,4-b]thiophene (**2.19**) using a Ni(0) complex (Ni(COD)₂, bipyridine, 1,5-cyclooctadiene, DMF) yielded a dark blue polymer which was only slightly soluble in CHCl₃ and THF. The UV-vis-NIR spectrum of the soluble portion of the polymer (CHCl₃ solution) showed a λ_{max} of 614 nm. Electrical conductivity of the pressed pellets was 1.4×10^{-6} S cm⁻¹ before doping and 2.9×10^{-6} S cm⁻¹ after doping with NOBF₄. No significant change in electrical conductivity was observed upon doping with FeCl₃.

Polymerization via 2-decylthieno[3,4-b]thiophene (**2.33**) using a FeCl₃ oxidative polymerization method yielded a polymer which was soluble in organic solvents such as CHCl₃ and THF. The polymer was bluish-green in color. The molecular weight was $M_n = 3.0 \times 10^4$ g mol⁻¹ determined by GPC using polystyrene standards. The UV-vis-NIR spectrum of the polymer solution (CHCl₃) showed a λ_{max} of 704 nm, which was 90 nm higher than the CHCl₃ solution of the soluble portion of the polymer from the Ni(0) polymerization. Upon doping with FeCl₃, the polymer solution showed two λ_{max} at 795 nm and 1350 nm while the λ_{max} at 704 nm diminished. The polymer film cast from CHCl₃ solution showed a λ_{max} of 738 nm without doping, which was 34 nm higher than the polymer solution. The longer conjugation length of polymer chains in the film compared with the polymer chains in solution is a typical property of conjugated polymers.¹⁷⁵ Upon doping with 0.1% FeCl₃ solution in methanol, the peak at 738 nm decreased gradually while a new peak at λ_{max} of 1052 nm was formed. The doping was reversible and NH₃ gas could be used to dedope the polymer films. No significant color change was observed upon doping with FeCl₃. The bandgap, from the band edge, was 1.2 eV which was 0.8-1.0 eV lower than the parent

polymer, polythiophene. Therefore, polymer 2.1 is a new processable low bandgap polymer. The bandgap obtained from the absorption maximum was 1.68 eV which was very close to the bandgap (1.5 -1.6 eV) from the theoretical calculations.¹³⁴ Electrical conductivities of the polymer films cast from CHCl₃ solution were 2.2×10^{-5} S cm⁻¹ without doping, 8.8×10^{-3} S cm⁻¹ after doping with I₂ and 7.2×10^{-2} S cm⁻¹ after doping with FeCl₃ in CH₃OH.

The polymer from synthetic route 3 using Ni(0) polymerization showed lower solubility, lower electrical conductivity and a lower UV-vis-NIR absorption maximum than the polymer from synthetic route 4 using FeCl₃ oxidative polymerization. Possible reasons may include: (1) sp³ defects were introduced into the polymer backbone during the Ni(0) polymerization so that the conjugation length was relatively low which could result in lower UV-vis-NIR absorption maximum and lower electrical conductivity; (2) cross-linking between polymer chains took place during the Ni(0) polymerization and formed a network structure, which could result in the lower solubility; (3) the low solubility of the polymer may be due to very high molecular weight of the polymer formed in the Ni(0) polymerization. The same phenomena was also observed by Miyazaki et al., in the Ni(0) polymerization of 3-dodecyl-2,5-diiodothiophene and high molecular weight was postulated as the reason with no other explanation was given.³¹

CHAPTER 3

EXPERIMENTAL

3.1 General

Infrared spectra were recorded on a Biorad-Digilab FTS-40 Fourier Transform Infrared instrument using powdered sample with KBr in a diffuse reflectance unit or liquid samples with NaCl plates and reported as \bar{v} in cm^{-1} with resolution of 8 cm^{-1} .

^1H NMR and ^{13}C NMR spectra were obtained on a Bruker MSL-300 spectrometer. ^1H NMR spectra were recorded at 300.13 MHz in CDCl_3 reported in ppm as δ relative to internal tetramethylsilane. ^{13}C NMR spectra were taken at 75.47 MHz in CDCl_3 and are reported in ppm relative to residual CHCl_3 at 77.00 ppm. The spectra were run at room temperature unless noted.

HPLC was carried out using a Waters 501 HPLC pump, a Lambda-Max Model 481 LC UV-vis detector at 254 nm and Maxima 820 Chromatography Software with an ECONOSIL C18 reverse-phase column (250 mm x 4.6 mm) with methanol as eluent with a flow rate of 1 mL/min. GC chromatograms were recorded on Varian model 3700 gas chromatograph with a silica capillary column of DB-5 (30 m long, 0.319 mm diameter, 0.025 μ coating thickness) with initial temperature of 80 °C for one minute and a heating rate of 10 °C/min. from 80 °C to 240 °C.

Elemental analysis were obtained on a Perkin-Elmer 2400 CHN analyzer or determined by Texas Analytical Laboratories, Stafford, Texas.

TGA were carried out on a DuPont 9900 Thermal Analysis system fitted with a Model 951 Thermogravimetric Analyzer. A typical TGA curve was recorded as the weight loss of the sample under a nitrogen atmosphere from 40 to 800 °C with a heating rate of 10 °C/min.

Gel permeation chromatography was carried out with a Waters Model 510 pump, Model 490 multiwavelength detector at 254 nm, Millennium 2010 Software, and a combination of 10^3 , 10^4 and 10^5 Å Ultrastyragel columns in series. The calibration curve was determined by use of polystyrene standards from a molecular weight of 800 to 9×10^5 g/mol. The carrier solvent used was tetrahydrofuran at a flow rate of 1 mL/min.

UV-vis-NIR spectra were recorded on a Cary 5E UV-vis-NIR spectrophotometer using CHCl₃ solution and polymer thin films cast onto quartz cuvettes from polymer solutions.

The polymer films or polymer pressed pellets were doped with FeCl₃, NOBF₄ or I₂. For FeCl₃ and NOBF₄ doping, the polymer samples were soaked in a 1% nitromethane solution at room temperature, 1 minutes for films and 1 hour for the pressed pellets. The doped films and pellets were washed with fresh nitromethane and dried before the electrical conductivity measurement. For I₂ doping, the polymer films were exposed to iodine vapor at room temperature for 24 hours, then excess iodine was pumped off under vacuum for 1 hour. The electrical conductivity of doped polymer thin films or pressed pellets was measured using the standard four-in-line probe method.^{2,170} The thickness of polymer films and pressed pellets was determined with a micrometer.

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Mg turnings were washed with diethyl ether and dried at 110 °C overnight. Commercially available n-BuLi (1.6 M in hexane), bromine, polyphosphoric acid, P₂S₅, P₄S₇, Lawesson's reagent, 3-thiophenealdehyde, 2-thiophenecarboxylic acid, SOCl₂,

hexadecyltributylphosphonium bromide (phase transfer agent), $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, n-dodecanal, sulfur and barium promoted copper chromite were used without further purification. Diethyl ether, THF, hexanes and benzene were dried over sodium benzophenone ketyl and freshly distilled prior to use. Methanol was distilled from Mg turnings and stored in a dry box. Thiophene, 1-bromodecane, 2,5-dichlorothiophene, triethylphosphite and quinoline were distilled and stored over 4A molecular sieves.

3.2 Synthesis

3-Thiophenealdehyde ethylene acetal (2.9). 3-Thiophenealdehyde ethylene acetal (2.9) was prepared according to the literature procedure^{138,146} in 64% yield. b.p. 54-55 °C (0.03-0.04 mm) [lit.¹⁴⁶ b.p. 82-84 °C (1.4 mm)].

2-Formyl-3-thiophenealdehyde ethylene acetal (2.10). 2-Formyl-3-thiophenealdehyde ethylene acetal (2.10) was prepared according to the literature procedure.¹⁴⁶ The product was used directly in the next step without purification.

2,3-Thiophenedialdehyde (2.11). 2,3-Thiophenedialdehyde (2.11) was prepared according to the literature procedure¹⁴⁶ in 51% total yield from 2-formyl-3-thiophenealdehyde ethylene acetal (2.10). m.p. 167-168 °C (lit.¹⁴⁶ m.p. 167 °C)

2,3-Bis(hydroxymethyl)thiophene (2.12). 2,3-Bis(hydroxymethyl)thiophene (2.12) was prepared according to the literature procedure¹⁴⁶ in 85% yield. The product was used directly in the next step without purification.

2,3-Bis(bromomethyl)thiophene (2.13). 2,3-Bis(bromomethyl)thiophene (2.13) was prepared according to the literature procedure¹⁴⁶ in 90% yield. m.p. 49-50 °C (lit.¹⁴⁶ m.p. 49-50 °C).

4,6-Dihydrothieno[3,4-b]thiophene (2.7). 4,6-Dihydrothieno[3,4-b]thiophene (2.7) was prepared according to the literature procedure¹⁴⁶ in 25% yield. Li₂S was also used instead of Na₂S to give 28% yield. bp 50 °C (0.2 mm) [lit.¹⁴⁶ b.p. 70.5-71 °C (0.7 mm)].

2-Bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8). 100 mg (0.7 mmol) of 4,6-dihydrothieno[3,4-b]thiophene (2.7) in 20 mL of CHCl₃ was treated with 120 mg (0.7 mmol) of Br₂ in 5 mL of CHCl₃. The orange color of bromine vanished in five minute. The CHCl₃ was removed under reduced pressure and the product was then recrystallized from hexane at -78 °C and dried under vacuum. Yield 70 mg (45%). m.p. 53-54 °C. ¹H NMR: δ: 6.79 (s, 1 H), 4.16-4.14 (m, 2H), 4.08-4.06 (m, 2 H); ¹³C NMR: δ: 142.0, 138.8, 124.7, 114.2, 34.2. Anal. Calcd. for C₆H₅S₂Br: C, 32.59; H, 2.28. Found: C, 32.27; H, 2.16.

Grignard coupling. This reaction was done under a N₂ atmosphere. The mole ratio between Mg, 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8) and the 1-bromodecane was 1:1:1. The concentration was 100 mg of 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8) in 10 mL of solvent and 156 mg of 1-bromodecane in 10 mL of solvent. Grignard reagents were made right before use. NiCl₂(dppp) was used as a catalyst in all cases. The mole ratio between NiCl₂(dppp) and 1-bromodecane or 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8) was 1:100. The catalyst was added after the addition of the bromo compound to the Grignard reagent. The reaction was followed by GC.

A. C₁₀H₂₁MgBr in dry ether was added to 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8) in dry ether. The reaction mixture was refluxed overnight and quenched with 1 N HCl.

B. C₁₀H₂₁MgBr in dry THF was added to 2-bromo-4,6-dihydrothieno[3,4-b]thiophene (2.8) in dry THF. The reaction mixture was refluxed overnight and quenched with 1 N HCl.

C. 4,6-Dihydrothieno[3,4-b]thiophene-2-magnesium bromide in dry ether was added to C₁₀H₂₁Br in dry ether. The reaction mixture was refluxed overnight and quenched with 1 N HCl.

D. 4,6-Dihydrothieno[3,4-b]thiophene-2-magnesium bromide in dry THF was added to C₁₀H₂₁Br in dry THF. The reaction mixture was refluxed overnight and quenched with 1 N HCl.

Of all the above conditions, no desired product was detected. GC was used to monitor the reactions.

2-Decylthiophene (2.15). 33 mL (52.8 mmol) of BuLi (1.6 M in hexanes) was dropped into a solution of 4.00 g (47.5 mmol) of thiophene in 20 mL of dry ether at room temperature. After refluxing for half an hour, 11.60 g (52.4 mmol) of decyl bromide in 20 mL of ether was then added dropwise. The reaction was followed by GC which showed the reaction was complete after refluxing for 2 days. The reaction mixture was quenched with 20 g of ice, then allowed to warm to room temperature. The organic layer was separated, and the aqueous layer was extracted with ether 3 times. The combined organic layer was dried over MgSO₄, the solvent was removed under reduced pressure and the residue was distilled under vacuum. b.p. 87-88 °C (0.03 mm). Yield 4.82 g (46%). ¹H NMR: δ: 7.08 (dd, J = 1.3 Hz, J = 5.1 Hz, 1H), 6.90 (dd, J = 3.4 Hz, J = 5.1 Hz, 1H), 6.78-6.75 (m, 1H), 2.80 (dt, J = 0.7 Hz, J = 7.3 Hz, 2H), 1.71-1.46 (quintet, J = 7.8 Hz, 2H), 1.26 (m, 14 H), 0.88 (t, J = 6.5 Hz, 2H); ¹³C NMR: δ: 145.8, 126.6, 123.8, 122.7, 31.9, 31.8, 29.9, 29.6, 29.4, 29.3, 29.2, 22.7, 14.1; Anal. Calcd. for C₁₄H₂₄S: C, 74.93; H, 10.78. Found: C, 75.03; H, 11.15.

Using TMEDA/hexane in the lithiation step increased the reaction rate (6 hours instead of 2 days) and gave a better yield (64%), but there were more side products as the product

from distillation had a purity of 92% compared to 99% when no TMEDA was used as determined by GC.

5-decyl-2,3-thiophenedicarboxylic acid (2.16). 0.42 g (1.87 mmol) of 2-decylthiophene (**2.15**) and 100 mL of dry THF were put into a 250 mL 3-necked reaction flask. 1.3 mL (2.08 mmol) of BuLi (1.6 M in hexanes) was added dropwise and the reaction mixture was stirred for half an hour. CO₂ gas was then continuously bubbled into the flask for half an hour. The reaction mixture was then refluxed for one hour to liberate the excess CO₂ gas. The reaction mixture was cooled to -78 °C by a Dry Ice / acetone bath, and the second part of the BuLi (1.8 mL, 1.6 M in hexanes, 2.88 mmol) was then added. After stirring for half an hour at -78 °C, CO₂ gas was again introduced into the reaction mixture. The reaction was stopped after 2 hours of CO₂ gas purge and the THF was removed under reduced pressure. 1N HCl was slowly added to the residue until precipitate formed. The mixture was extracted with 20 mL of ether (This portion of organic layer contained mostly **2.18**). The water layer was then acidified with 5 mL of 1 N HCl and extracted with 20 mL portions of ether 3 times (This portion of organic layer contained mostly **2.16**), and the water layer was saturated with NaCl and again extracted twice with ether. The combined ether solution of the portion which contained mostly **2.16** was dried over MgSO₄. The ether was removed from the combined organic layer under reduced pressure. The residue was recrystallized from water and then from hexane. Yield 0.36 g (61%). m.p. 64-66 °C. ¹H NMR (run at 60 °C): δ: 8.60 (broad, 2 H), 7.43 (s, 1 H), 2.80 (t, J = 8 Hz, 2 H), 1.69 (quintet, J = 7 Hz, 2 H), 1.27 (m, 14 H), 0.87 (t, J = 6 Hz, 3 H); ¹³C: δ: 166.7, 164.9, 153.3, 136.1, 134.3, 130.1, 31.9, 31.0, 30.1, 29.5, 29.4, 29.3, 29.2, 28.9, 22.7, 14.1; IR: ν: 3344, 2950, 2924, 2853, 2597, 2480, 1887, 1694, 1631, 1612, 1535, 1471, 1374, 1255, 1091, 955, 866, 757, 722, 651, 601, 499, 455 cm⁻¹; Anal. Calcd. for C₁₆H₂₄SO₄: C, 61.51; H, 7.74. Found: C, 61.41; H, 7.88.

5-decyl-2-thiophenecarboxylic acid (2.18). This is a side product formed during the synthesis of 2.16. The ether layer from the previous extraction was dried over MgSO₄ and ether was removed under reduced pressure. The residue was recrystallized from water and then from hexane. m.p. 83-84 °C. Yield 0.15 g (30%). ¹H NMR (run at 60 °C): δ: 10.17 (broad, 1 H), 7.70 (d, J = 3 Hz, 1 H), 6.81 (d, J = 3 Hz, 1 H), 2.84 (t, J = 8 Hz, 2 H), 1.70 (quintet, J = 7 Hz, 2 H), 1.27 (m, 14 H), 0.88 (t, J = 6 Hz, 3 H); ¹³C: δ: 166.5, 135.2, 129.5, 125.5, 31.9, 31.3, 30.5, 29.5, 29.3, 29.0, 22.6, 14.1; IR: ν: 3350, 3107, 2952, 2918, 2850, 2673, 2552, 1677, 1590, 1543, 1466, 1425, 1343, 1292, 1232, 1112, 1043, 1033, 938, 822, 753, 732, 689, 627, 565, 514, 502, 474 cm⁻¹; Anal. Calcd. for C₁₅H₂₄SO₂: C, 67.17; H, 9.01. Found: C, 66.98; H, 8.86.

5-Decyl-2,3-thiophenedicarboxylic thioanhydride (2.14). 100 mg (0.32 mmol) of 5-decyl-2,3-thiophenedicarboxylic acid (2.16) and 1 mL of SOCl₂ were mixed together and stirred overnight. The SOCl₂ was then removed under vacuum, and the crude product was directly used in the next step.

Into 2 mL of methylene chloride, the crude 5-decyl-2,3-thiophenedicarboxylic chloride (2.17) made above and 10 mg (2.0 mmol) of hexadecyltributylphosphonium bromide (phase transfer agent) were put and the mixture was cooled to 0 °C. 76 mg (3.2 mmol) of Na₂S·9H₂O was added to the reaction mixture which was then stirred for 3 hours. The reaction mixture was run through a short silica gel column to remove the phase transfer agent. The methylene chloride was removed, and the product was dried under vacuum to give 61 mg (62%) of the product. The purity of the product was determined by HPLC (purity > 99.9%). m.p. 58-59 °C. ¹H NMR: δ: 7.08 (t, J = 0.9 Hz, 1H), 2.90 (dt, J = 0.8 Hz, J = 7.5 Hz, 2H), 1.73 (quintet, J = 7.5 Hz, 2H), 1.28 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H); ¹³C NMR: δ: 183.5, 180.6, 163.4, 151.6, 145.5, 118.6, 31.8, 31.5, 31.1, 29.4, 29.3, 29.2, 28.9, 22.7, 14.1; IR: ν: 3400, 3152, 3094, 2951, 2915, 2848, 1770, 1685, 1593, 1525, 1460, 1402, 1238, 1138,

1022, 1007, 870, 726, 638, 568, 510 cm⁻¹; Anal. Calcd. for C₁₆H₂₂S₂O₂: C, 61.90; H, 7.14. Found: C, 61.62; H, 7.22.

Polymerization of 5-decyl-2,3-thiophenedicarboxylic thioanhydride. 1 g of monomer **2.14** was refluxed under N₂ in 5 mL of P(OEt)₃. After 48 hours, the reaction was stopped. No precipitate was formed upon cooling to room temperature. 10 mL of methanol was then added to the reaction mixture, and a precipitate formed. The dark red precipitate was filtered and washed with methanol. Yield 0.2 g of solid. This solid is a low molecular weight material as indicated by GPC of the CHCl₃ solution which showed the molecular weight to be lower than 500 g mol⁻¹. The ¹H NMR spectrum of the solid showed the long decyl chain (broad) and a broad aromatic peak at ~7.0 ppm and a sharp peak at 7.32 ppm. Three peaks above 9 ppm were also observed.

2-Bromo-n-dodecanal (2.21). 20.00 g (109 mmol) of n-dodecanal in 400 mL of chloroform was put in a 1000 mL three-necked flask equipped with a condenser and a dropping funnel. 4.4 mL (85.4 mmol) of bromine in 400 mL of chloroform was dropped in the reaction flask at such a rate as the color of the bromine diminished immediately after the addition. The reaction progress could be monitored by GC (GC retention time for n-dodecanal was around 7 minutes and for 2-bromo-n-dodecanal was around 9.5 minutes). After the addition, the reaction mixture was stirred for half an hour. The reaction mixture was then poured into 100 mL of cold saturated NaHCO₃, and the organic layer was separated and washed twice with 30 mL portions of water. The organic layer was then dried over Na₂SO₄ and the solvent was removed under reduced pressure. The remaining crude product was then distilled under vacuum. b.p. 93 °C (0.03 mm). Yield 20 g (70%). ¹H NMR: δ: 9.43 (d, J = 3 Hz, 1 H), 4.21 (m, 1 H), 1.96 (m, 2 H), 1.26 (m, 16 H), 0.88 (t, J = 6 Hz, 3 H); ¹³C NMR: δ: 192.6, 55.4, 31.8, 31.6, 29.5, 29.4, 29.2, 28.9, 26.9, 22.6, 14.1; Anal. Calcd. for C₁₂H₂₃OBr: C, 54.76; H, 8.81. Found: C, 54.99; H, 9.20.

2-Bromo-1,1-dimethoxydodecane (2.22). 6.00 g (22.8 mmol) of 2-bromo-n-dodecanal (2.21) and 0.88 g (5 mmol) of benzenesulfonic acid was refluxed in 200 mL of dry methanol for 4 hours under N₂. The reaction mixture was then cooled to room temperature. Methanol was removed under reduced pressure and 20 mL of saturated NaHCO₃ was added to the reaction mixture. The mixture was then extracted with 50 mL of ether 3 times. The combined ether layer was washed with 20 mL of water and 20 mL of saturated NaHCO₃ and then with 20 mL portions of water 3 times. The ether layer was dried over Na₂SO₄ and filtered. The ether was removed under reduced pressure. The residue was then distilled under vacuum. b.p. 90-91 °C (0.01 mm). Yield 5.95 g (84%). ¹H NMR: δ: 4.38 (d, J = 5 Hz, 1 H), 3.97 (m, 1 H), 3.45 (s, 6 H), 1.89 (m, 1 H), 1.74 (m, 1 H), 1.60 (m, 1 H), 1.26 (m, 15 H), 0.88 (t, J = 6 Hz, 3 H); ¹³C NMR: δ: 106.2, 55.4, 55.0, 54.9, 32.8, 31.9, 29.6, 29.4, 29.3, 29.0, 27.3, 22.7, 14.1; Anal. Calcd. for C₁₄H₂₉O₂Br: C, 54.37; H, 9.45. Found: C, 54.57; H, 9.81.

1,1-Dimethoxydodecyl-2-disulfide (2.23). The reaction was run according to literature procedure with a little modification.¹⁶⁰ 0.468 g (15 mmol) of sulfur and 2.34 g (9.74 mmol) of Na₂S·9H₂O were mixed with 40 mL of ethanol in a three-necked flask and stirred for half an hour. 4.00 g (12 mmol) of 1,1-dimethoxy-2-bromododecane (2.22) and 0.108 g (0.65 mmol) KI were then added to the reaction mixture. The reaction mixture was refluxed overnight. The solvent was removed under reduced pressure to 5 mL. Water was then added to the mixture and the mixture was extracted with ether 3 times. The ether layer was dried over MgSO₄, and removed under reduced pressure. The crude product was used directly in the next step because of the difficulty of purification.

2,5-Dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20). This reaction was done in a N₂ environment. LDA was made as follows: 0.79 g (7.8 mmol) of diisopropyl amine was put in a 25 mL flask and 10 mL of freshly distilled THF was added.

4.8 mL (7.68 mmol) of BuLi (1.6 M in hexanes) was added dropwise with stirring. 1.08 g (7.06 mmol) of 2,5-dichlorothiophene was dissolved in 40 mL of THF and cooled to -78 °C using an acetone / Dry Ice bath. The LDA solution was then added to the cooled flask very slowly. After stirring for half an hour, the crude disulfide (2.23) made from the previous reaction in 25 mL of dry THF was added to the reaction mixture very slowly. The reaction mixture was stirred for two hours at -78 °C and then warmed to room temperature. THF was removed under reduced pressure. 5 mL of water was added to the residue and the mixture was then extracted with ether 3 times. The combined ether layer was dried with MgSO₄ and the ether was removed under reduced pressure. The product was purified by a silica gel column (hexane: ethyl acetate, 100:1). Yield 1.05 g (36%). ¹H NMR: δ: 6.84 (s, 1 H), 4.30 (d, J = 5 Hz, 1 H), 3.42 (s, 3 H), 3.38 (s, 3 H), 3.06 (m, 1 H), 1.74 (m, 2 H), 1.44 (m, 2 H), 1.26 (m, 14 H), 0.89 (t, J = 6 Hz, 3 H); ¹³C NMR: δ: 130.4, 129.1, 128.7, 125.8, 107.0, 55.3, 52.6, 31.9, 29.6, 29.4, 29.3, 26.8, 22.7, 14.1; Anal. Calcd. for C₁₈H₃₀S₂O₂Cl₂: C, 52.29; H, 7.31; Found: C, 52.34; H, 7.30.

2,5-Dichloro-3-[2-(1-methoxydodecanyl)thio]thiophene (2.26). This is a side product during the synthesis and purification process of 2.20. This product was also purified with a silica gel column (hexane: ethyl acetate, 100:1). Yield 0.1 g (4%) ¹H NMR: δ: 6.64 (s, 1 H), 6.54 (s, 1 H), 3.69 (s, 3 H), 2.15 (t, J = 7 Hz, 2 H), 1.44 (m, 2 H), 1.25 (m, 14 H), 0.88 (t, J = 6 Hz, 3 H); ¹³C NMR: δ: 152.9, 131.2, 127.6, 126.0, 122.8, 110.8, 60.2, 31.9, 29.6, 29.4, 28.9, 27.4, 22.7, 14.1; Anal. Calcd. for C₁₇H₂₆S₂OCl₂: C, 53.53; H, 6.87; Found: C, 53.88; H, 7.17.

4,6-Dichloro-2-decyli Thieno[3,4-b]thiophene (2.19). 2.00 g (4.83 mmol) of 2,5-dichloro-3-[2-(1,1-dimethoxydodecyl)thio]thiophene (2.20) and 10 mL of benzene were put in a flask. 20.00 g of polyphosphoric acid (PPA) was weighed into the flask. The mixture was refluxed in an oil bath for 4 days. The reaction mixture was then cooled to room

temperature and the benzene layer was poured off and the PPA layer was washed with benzene 3 times. The combined benzene layer was then washed with NaHCO_3 once and H_2O 3 times. The organic layer was dried with MgSO_4 and the benzene was removed under reduced pressure. The product was purified with a silica gel column (hexanes as an eluent). Yield 0.39 g (23%). The purity of the product was determined by HPLC (purity: 99.9%). ^1H NMR: δ : 6.46 (t, $J = 1.1$ Hz, 1H), 2.71 (dt, $J = 1.1$ Hz, $J = 7.7$ Hz, 2 H), 1.67 (quintet, 2 H), 1.26 (m, 14 H), 0.88 (t, 3 H); ^{13}C NMR: δ : 154.7, 143.7, 135.8, 112.4, 111.5, 110.5, 31.9, 31.9, 30.0, 29.6, 29.5, 29.3, 29.0, 22.7, 14.1; IR: $\bar{\nu}$: 2955, 2926, 2854, 1541, 1466, 1330, 1103, 971, 850, 810 cm^{-1} ; Anal. Calcd. for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{S}_2$: C: 55.01; H: 6.35. Found: C: 55.34; H: 6.40.

2-Chloro-5-decylthieno[3,2-b]thiophene (2.25). This is a side product during the synthesis and purification of **2.19**. Yield 0.14 g (9%). The product was also purified with a silica gel column (hexanes). m.p. 39.5-40.5 °C. ^1H NMR: δ : 7.05 (d, $J = 0.6$ Hz, 1 H), 6.83 (m, 1 H), 2.84 (dt, $J = 0.8$ Hz, $J = 7.5$ Hz, 2 H), 1.69 (quintet, $J = 7.4$ Hz, 2 H), 1.26 (m, 14 H), 0.88 (t, $J = 6.2$ Hz, 3 H); ^{13}C NMR: δ : 147.7, 136.0, 134.8, 129.0, 118.8, 116.0, 31.9, 31.5, 30.8, 29.6, 29.5, 29.3, 29.0, 22.7, 14.1; Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{ClS}_2$: C: 61.02; H: 7.36. Found: C: 61.38; H: 7.75.

2-Decylthieno[3,2-b]thiophene (2.29). 0.1 g (0.32 mmol) of 2-chloro-5-decylthieno[3,2-b]thiophene (**2.25**) and 4 mL of freshly distilled THF was put in a 10 mL of three-necked flask which fitted with a N_2 inlet. 1 mL (1.6 mmol) of n-BuLi was added in the reaction flask dropwise while the reaction mixture was cool to 0 °C with an ice bath. The reaction mixture was then warmed up to room temperature and stirred for one hour. The reaction mixture was then quenched with 2 mL of water and extracted with 10 mL of ether. The ether layer was separated and dried with MgSO_4 . Ether was then removed under reduced pressure. The residue was run through a silica gel column with hexane as an eluent to yield

0.08 g of 2-decylthieno[3,2-b]thiophene. ^1H NMR: δ : 7.24 (d, J = 5.3 Hz, 1 H), 7.16 (dd, J = 0.5 Hz, J = 5.3 Hz, 1 H), 6.94 (m, 1 H), 2.86 (dt, J = 0.7 Hz, J = 7.3 Hz, 2 H), 1.70 (quintet, 2 H), 1.26 (m, 14 H), 0.88 (t, J = 6.4 Hz, 3 H); ^{13}C NMR: δ : 148.6, 138.7, 137.3, 125.2, 119.4, 116.1, 31.9, 31.6, 31.2, 30.0, 29.6, 29.3, 29.1, 22.7, 14.1; Anal. Calcd. for : $\text{C}_{16}\text{H}_{24}\text{S}_2$: C, 68.52; H, 8.62. Found: C, 68.87; H, 8.89.

Attempted polymerization of 4,6-dichloro-2-decylthieno[3,4-b]thiophene (2.19) through Grignard coupling:

Attempt I: In a three-necked flask equipped with a N_2 inlet, a condenser, a magnetic stirrer and a rubber septum was added 7 mg (0.29 mg-atom) of Mg tuning. 0.1 g (0.29 mmol) of 4,6-dichloro-2-decylthieno[3,4-b]thiophene (2.19) in 2 mL of freshly distilled THF was slowly injected into the reaction flask. The reaction mixture was refluxed for 12 hours. No reaction was observed between the Mg and 2.19 since the amount of Mg did not reduce significantly during refluxing and GC showed recovery of 2.19 when the reaction mixture was quenched with H_2O .

Attempt II: In a three-necked flask equipped with a N_2 inlet, a condenser and a rubber septum was added 0.1 g (0.29 mmol) of 4,6-dichloro-2-decylthieno[3,4-b]thiophene (2.19) in 1 mL of THF. The flask was cooled down to 0 °C by an ice bath and 0.2 mL (0.34 mmol) of BuLi (1.6 M in hexanes) was added. The reaction mixture was warmed to room temperature and stirred for another half an hour at room temperature. 77 mg (0.3 mmol) of $\text{MgBr}_2\cdot\text{OEt}_2$ in 1 mL of THF was then slowly dropped in the reaction mixture. The reaction mixture was then refluxed for half an hour. 1 mg (0.002 mmol) of $\text{NiCl}_2(\text{dppp})$ was added to the formed Grignard reagent to catalyze the Grignard coupling. The reaction mixture was refluxed and followed by TLC. The reaction was quenched with 1 N HCl after refluxing for 24 hours. TLC showed that the residue was a mixture of starting material 2.19 and 4-chloro-2-decylthieno[3,4-b]thiophene (or 6-chloro-2-decylthieno[3,4-b]thiophene).

Polymerization of 4,6-dichloro-2-decylthieno[3,4-b]thiophene. 0.472 g (1.72 mmol) of Ni(cyclooctadiene)₂ (Ni(COD)₂), 0.155 g (1.43 mmol) of 1,5-cyclooctadiene, 0.268 g (1.72 mmol) of 2,2'-bipyridine, and 10 mL of dimethylformamide (DMF) was mixed in a flask in a dry box. 0.5 g (1.43 mmol) of 4,6-dichloro-2-decylthieno[3,4-b]thiophene (**2.19**) was added to the reaction mixture. The flask was taken out of the dry box and connected to a N₂ inlet. The reaction mixture was heated to 80 °C and stirred for 48 hours. The reaction mixture was then cooled to room temperature and filtered. The precipitate was washed with methanol, acidic EDTA (pH = 4), basic EDTA (pH = 9) and water. The solid polymer was then dried under vacuum for 16 hours. Yield 0.363 g (91%) of the dark blue polymer. The solubility of the polymer in CHCl₃, THF and dichlorobenzene was very poor. UV-vis-NIR of the soluble part in CHCl₃ solution: $\lambda_{\text{max}} = 614 \text{ nm}$. ¹H NMR: δ: 1.88 (broad), 1.26 (broad), 0.88 (broad); IR: ν: 2951, 2923, 2851, 1650, 1554, 1461, 1437, 1267, 1081, 811, 721, 652 cm⁻¹; Conductivity (undoped): $1.4 \times 10^{-6} \text{ S cm}^{-1}$; (doped with NOBF₄): $2.9 \times 10^{-6} \text{ S cm}^{-1}$; Anal. Calcd. for polymer with no chlorine end groups (C₁₆H₂₂S₂): C: 69.01; H: 7.96. Found: C: 65.28; H: 7.34; Cl: 0.00.

The unreacted residue weighed 0.061 g and was identified as a mixture of 4,6-dichloro-2-decylthieno[3,4-c]thiophene (**2.19**), 4-chloro-2-decylthieno[3,4-b]thiophene (or 6-chloro-2-decylthieno[3,4-b]thiophene) and 2-decylthieno[3,4-b]thiophene (**2.33**) by TLC.

3-[2-(1,1-Dimethoxydodecyl)thio]-2-thiophenecarboxylic Acid (**2.34**). 2 g (15.6 mmol) of 2-thiophenecarboxylic acid was dissolved in 500 mL of dry THF and was cooled to -78 °C. 21 mL (33.6 mmol) of BuLi (1.6 M in hexanes) was injected into the cold 2-thiophenecarboxylic acid solution very slowly. The reaction mixture was stirred at -78 °C for one hour. Then the disulfide **2.23** which was made from 10 g (32.3 mmol) of 1,1-dimethoxy-2-bromododecane was dissolved in 50 mL of THF and slowly injected into the reaction mixture. The reaction mixture was stirred at -78 °C for one hour and then warmed to

room temperature. The THF was removed under reduced pressure. 30 mL of water and 50 mL of ether was added to the residue and the two layers were separated. The water layer was acidified with 6 N HCl and extracted with diethyl ether. The extract was then dried over MgSO₄ and filtered. The ether was removed under reduced pressure. 20 mL of hexanes was added to the residue and the mixture was put in a freezer (-15 °C). The crystals which formed were filtered and washed with 10 mL of cold hexanes. Yield 2.36 g (38%). m.p. 104-106 °C. ¹H NMR: δ: 10.88 (broad, 1 H), 7.56 (d, J = 5 Hz, 1 H), 7.13 (d, J = 5 Hz, 1 H), 4.35 (d, J = 5 Hz, 1 H), 3.44 (s, 3 H), 3.41 (s, 3 H), 3.3 (m, 1 H), 1.25-1.9 (m, 18 H), 0.88 (t, 3 H); ¹³C NMR: δ: 166.1, 143.5, 132.0, 129.2, 124.8, 107.4, 56.4, 55.8, 51.7, 31.9, 29.6, 29.4, 29.3, 27.0, 22.7, 14.1; Anal. Calcd. for C₁₉H₃₂O₄: C, 58.73; H, 8.30. Found: C, 58.39; H, 8.59.

3-[(1-Formylundecyl)thio]-2-thiophenecarboxylic Acid (2.35). This is a side product during the synthesis and the purification of 2.34. An analytical sample of 2.35 was obtained by stirring a hexanes solution of 2.34 at room temperature for one hour. ¹H NMR: δ: 10.27 (broad, 1 H), 9.27 (d, J = 10 Hz, 1 H), 7.58 (d, J = 5 Hz, 1 H), 7.08 (d, J = 5 Hz, 1 H), 3.78 (m, 1 H), 1.51 (m, 2 H), 1.27 (m, 12 H), 0.89 (t, J = 6 Hz, 3 H); ¹³C NMR: δ: 196.1, 167.1, 142.2, 133.1, 127.4, 123.1, 54.6, 31.9, 29.5, 29.4, 29.2, 28.1, 26.9, 22.7, 14.1; Anal. Calcd. for C₁₇H₂₆O₃: C, 59.61; H, 7.65. Found: C, 59.92; H, 7.65.

2-Decyl-6-thieno[3,4-b]thiophenecarboxylic Acid (2.36). 1 g (2.57 mmol) of 3-[2-(1,1-dimethoxydodecyl)thio]-2-thiophenecarboxylic acid (2.34) and 5 mL of benzene were put in a flask. 10.00 g of polyphosphoric acid (PPA) was weighed into the flask and the mixture was refluxed for 4 hours. The reaction mixture was then cooled to room temperature, the benzene layer was poured out and the PPA layer was washed with benzene 3 times. The combined benzene layer was then washed with H₂O three times. The organic layer was dried with MgSO₄ and the benzene was removed under reduced pressure. The product was purified

by running through a silica gel column (hexanes/ethyl acetate: 4/1). Yield: 358 mg (43%). ^1H NMR: δ : 10.0 (broad, 1 H), 7.49 (s, 1 H), 6.66 (s, 1 H), 2.80 (t, J = 7 Hz, 2 H), 1.72 (quintet, J = 7 Hz, 2 H), 1.26 (m, 14 H), 0.88 (t, J = 6 Hz, 3 H); ^{13}C NMR: δ : 167.8, 154.8, 147.8, 147.4, 119.8, 116.4, 113.2, 31.9, 31.7, 30.3, 29.6, 29.5, 29.3, 29.1, 22.7, 14.1; Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{S}_2\text{O}_2$: C, 62.92; H, 7.45. Found: C, 62.57; H, 7.69.

2-Decylthieno[3,2-b]thiophene (2.29). This is a side product during the synthesis and purification of 2.30 with 0.21 g (29%) yield. This product has the same ^1H and ^{13}C NMR spectra as the product from the BuLi treatment of 2.25 with structure of 2.29.

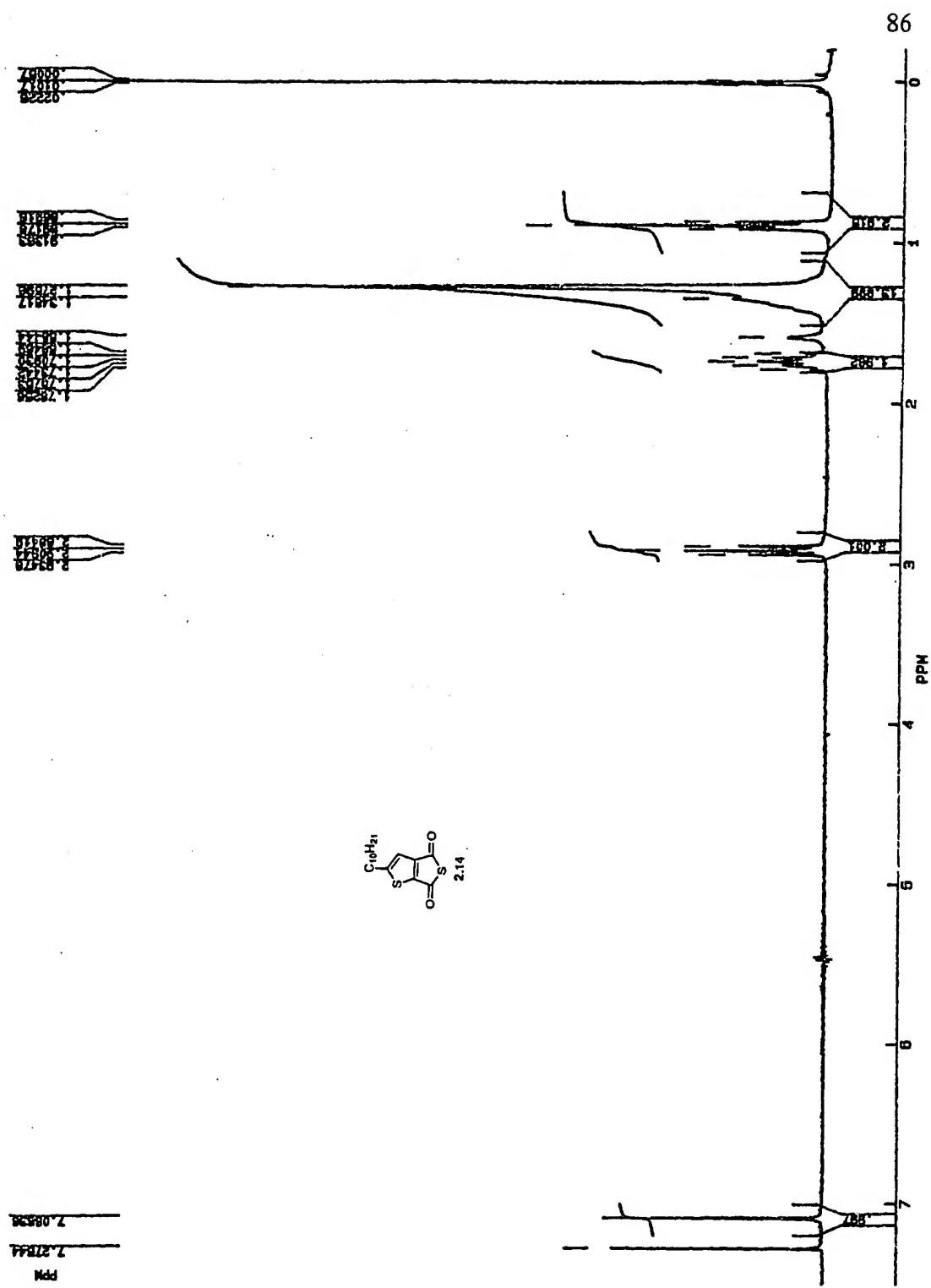
2-Decylthieno[3,4-b]thiophene (2.33). 0.2 g (0.62 mmol) of 2-decylthieno[3,4-b]thiophene-4-carboxylic acid (2.36) was dissolved in 2 mL of quinoline. 0.1 g of barium promoted copper chromite was put in the reaction mixture and the reaction mixture was kept under N_2 . The reaction mixture was refluxed for 20 minutes and the solid was filtered. The organic layer was washed with 1 N HCl three times, saturated NaHCO_3 three times and water 3 times. The organic layer was then dried over MgSO_4 and filtered. Benzene was removed under reduced pressure. The residue was run through a silica gel column with hexanes as eluent to yield 0.15 g (89%) of product. The purity of the product was determined by HPLC (purity > 99.9%). ^1H NMR: δ : 7.09 (s, 2 H), 6.57 (t, J = 0.9 Hz, 1 H), 2.72 (dt, J = 0.9 Hz, J = 7.7 Hz, 2 H), 1.67 (quintet, J = 7.6 Hz, 2 H), 1.26 (m, 14 H), 0.88 (t, J = 6.4 Hz, 3 H); ^{13}C NMR: δ : 152.9, 147.5, 138.7, 113.1, 110.1, 109.9, 31.9, 30.3, 29.5, 29.3, 29.1, 22.7, 14.1; IR: $\bar{\nu}$: 3107, 2954, 2924, 2853, 1570, 1464, 1435, 1378, 837, 814, 745, 503 cm^{-1} ; Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{S}_2$: C, 68.52; H, 8.62. Found: C, 68.59; H, 8.82.

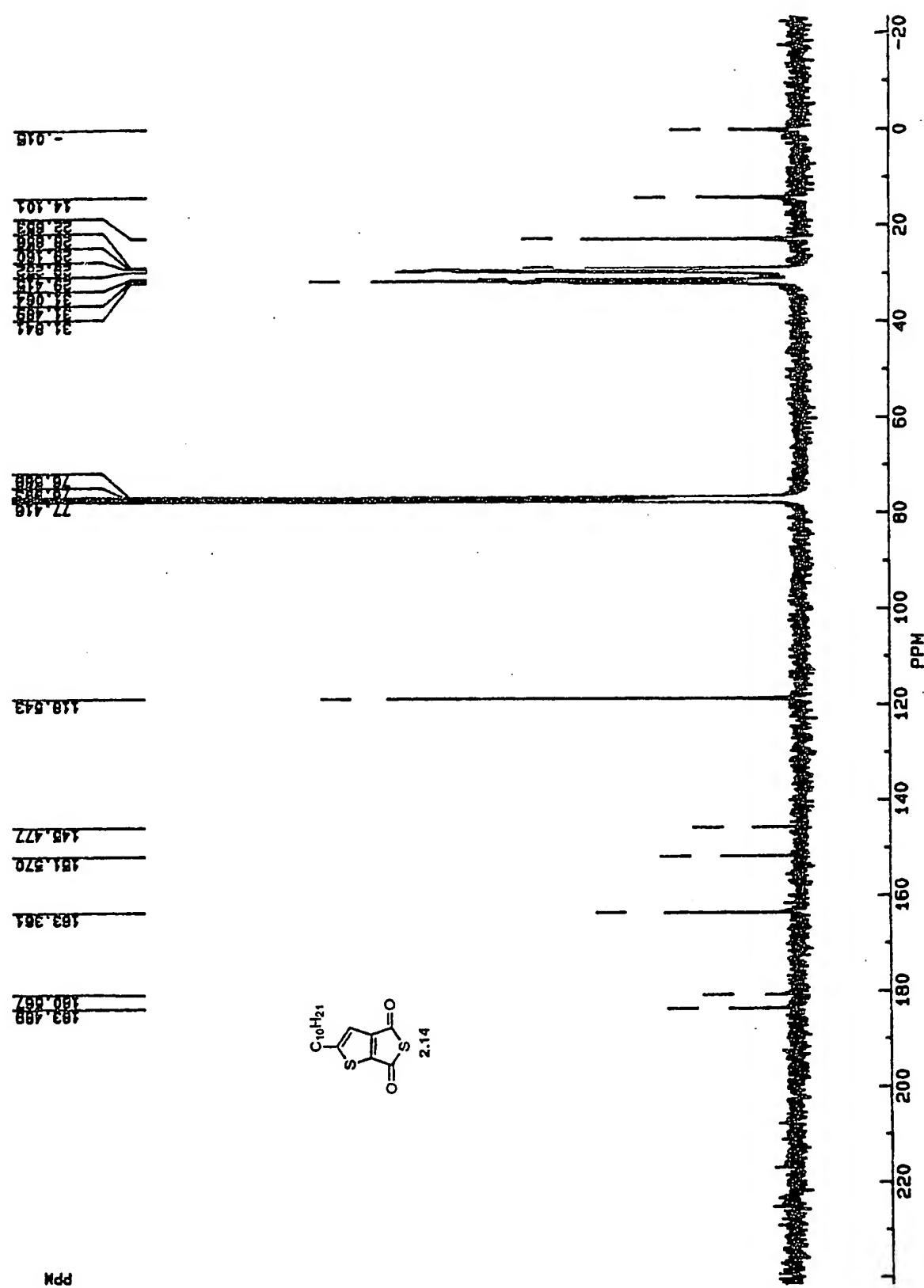
Polymerization of 2-decylthieno[3,4-b]thiophene. 100 mg (0.36 mmol) of 2-decylthieno[3,4-b]thiophene (2.33) in 2 mL of CHCl_3 was put in a 3-necked flask equipped with a N_2 inlet and an addition funnel. 57 mg (0.36 mmol) of FeCl_3 in 2 mL of CHCl_3 was

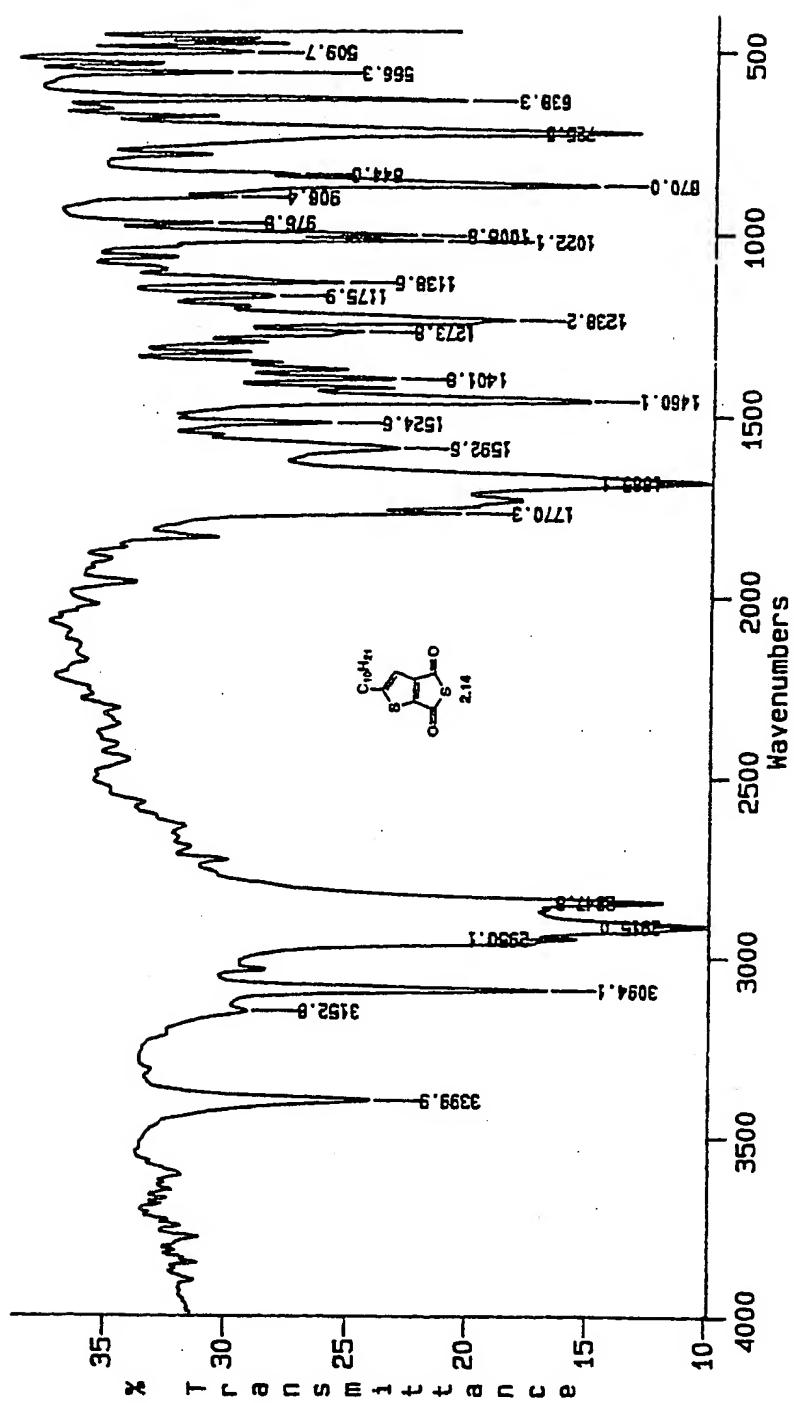
dropped in the reaction flask very slowly over half an hour. The reaction mixture turned purple on the addition of the first drop of FeCl_3 . The reaction mixture was stirred at room temperature for another hour and poured into 200 mL of methanol. A precipitate formed which was filtered under N_2 . The solid was dissolved in CHCl_3 and reprecipitated with methanol. The greenish-blue precipitate was filtered and dried under vacuum overnight to yield 81 mg (81%) of poly(2-decylthieno[3,4-b]thiophene) (2.1). The polymer was very unstable in room temperature. It turned to dark gray upon standing at room temperature. The polymer was dedoped with hydrazine monohydrate. 20 mg of the polymer was dissolved in 20 mL of CHCl_3 and this solution was extracted with 10 mL of hydrazine monohydrate three times. The organic layer was then dried over MgSO_4 and filtered. The CHCl_3 was removed under reduced pressure. The polymer was dried under vacuum for 16 hours. ^1H NMR: δ : 6.64, 2.69, 1.73, 1.26, 0.88; IR: $\bar{\nu}$: 3033, 2957, 2922, 2851, 1464, 1431, 1296, 1263, 1188, 1083, 1023, 979, 908, 846, 803, 721, 654, 584, 480 cm^{-1} ; UV-vis-NIR: CHCl_3 solution: $\lambda_{\text{max}} = 704 \text{ nm}$ (dedoped), $\lambda_{\text{max}} = 795 \text{ nm}$ and 1350 nm (doped with FeCl_3); film: $\lambda_{\text{max}} = 738 \text{ nm}$ (dedoped), $\lambda_{\text{max}} = 1052 \text{ nm}$ (doped with FeCl_3). Conductivity (dedoped): $2.2 \times 10^{-5} \text{ S cm}^{-1}$; (doped with I_2): $8.8 \times 10^{-3} \text{ S cm}^{-1}$; (doped with FeCl_3): $7.2 \times 10^{-2} \text{ S cm}^{-1}$. Molecular weight of the polymer determined by GPC showed the polymer had $M_n = 3.0 \times 10^4 \text{ g mol}^{-1}$ and $M_w = 4.3 \times 10^4 \text{ g mol}^{-1}$ with a polydispersity of 1.4. GPC also had two small peaks at very high molecular range ($>10^6 \text{ g mol}^{-1}$).

APPENDIX I

^1H NMR, ^{13}C NMR AND IR SPECTRA OF 5-DECYL-
2,3-THIOPHENEDICARBOXYLIC
THIOANHYDRIDE (2.14)



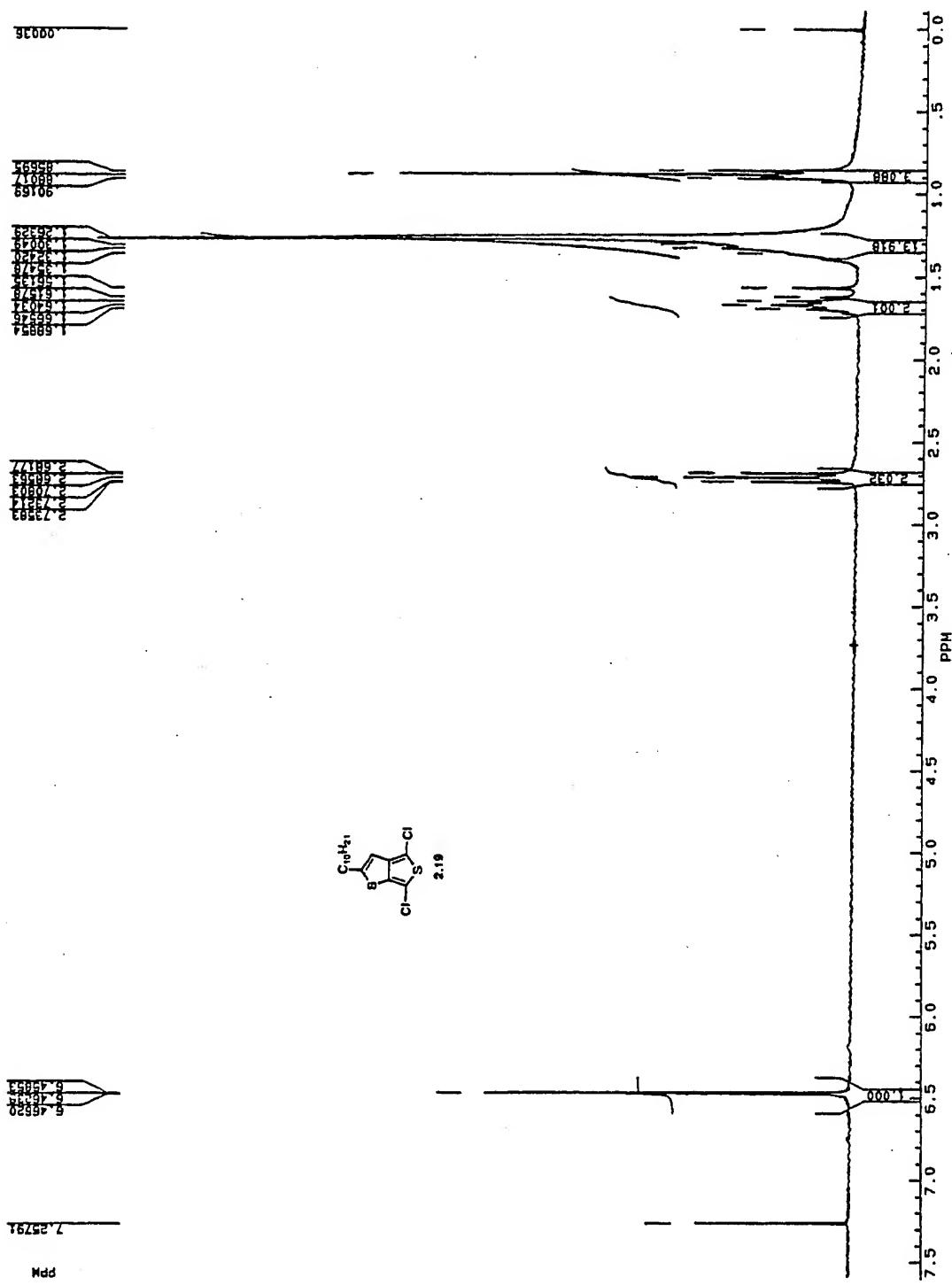


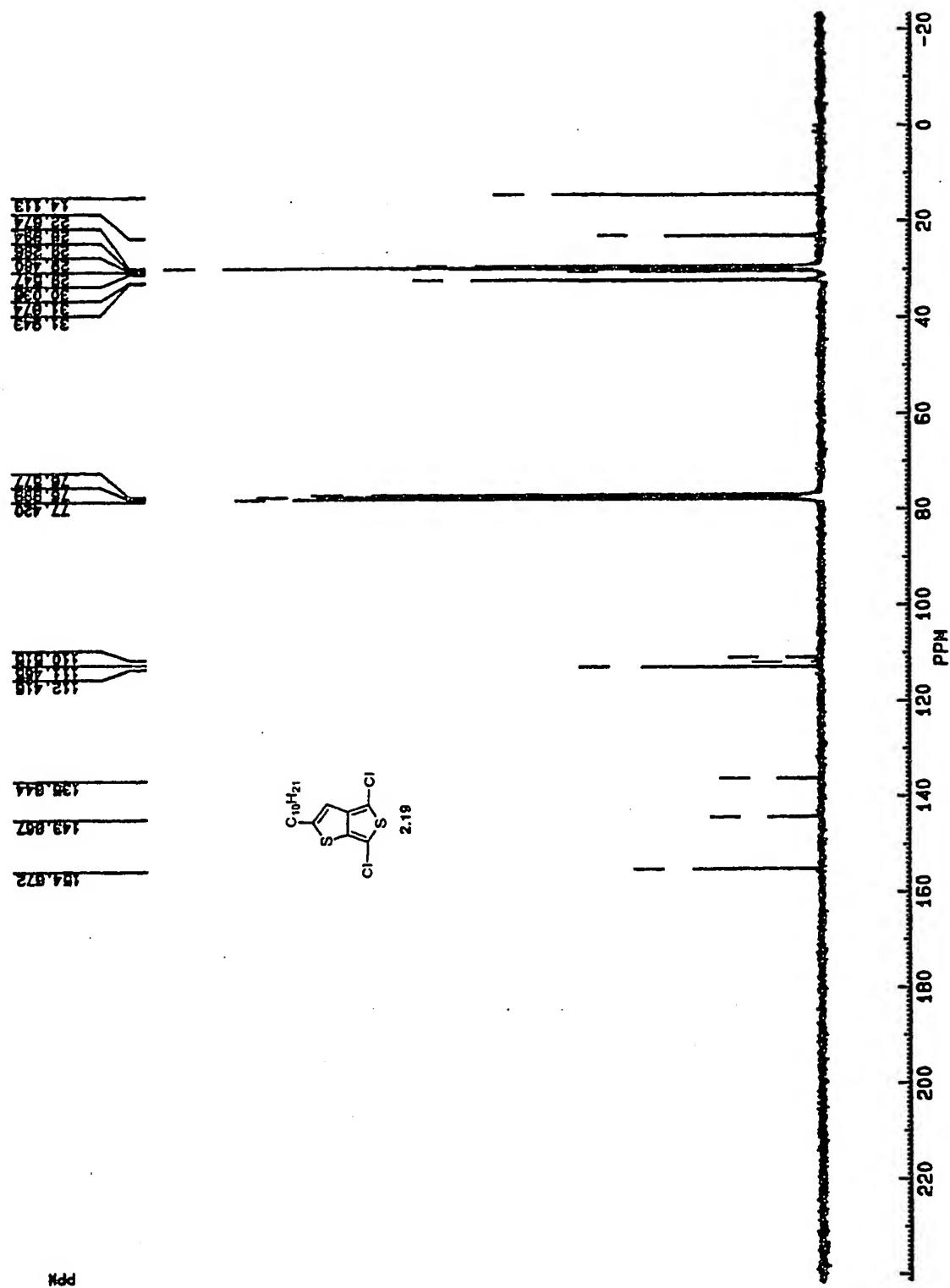


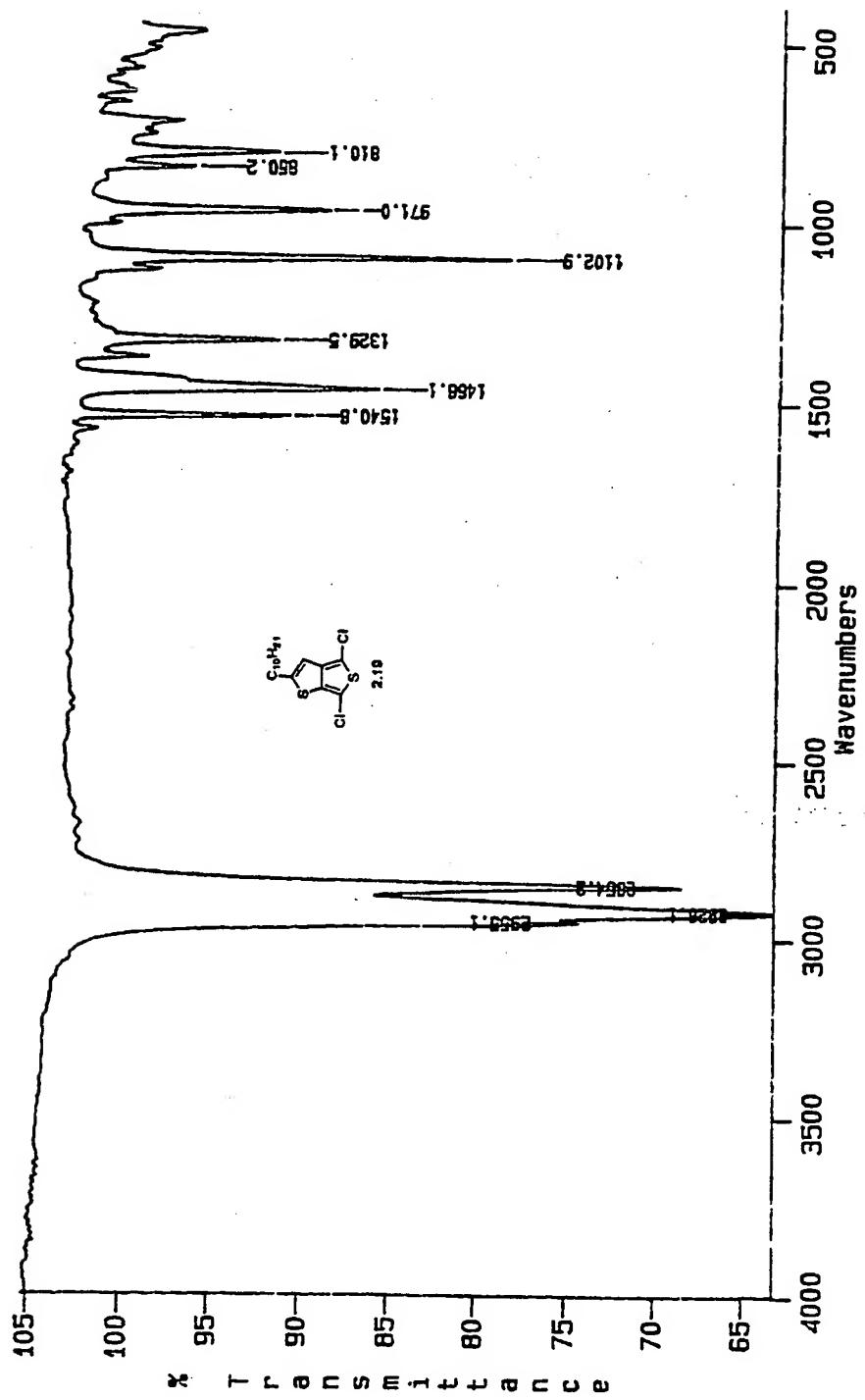
APPENDIX II

¹H NMR, ¹³C NMR AND IR SPECTRA OF 4,6-DICHLORO-
2-DECYLTHIENO[3,4-b]THIOPHENE (2.19)

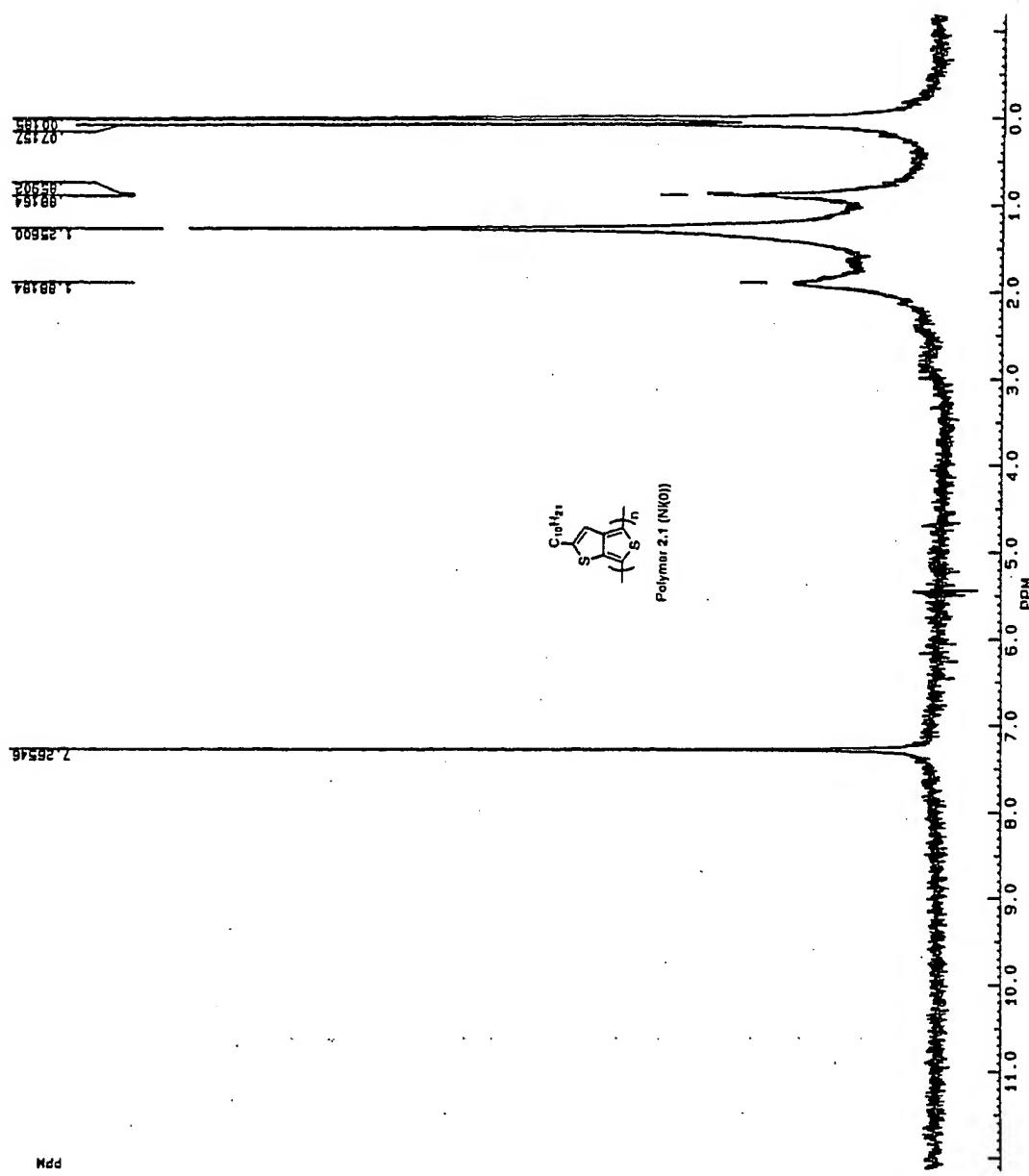
90

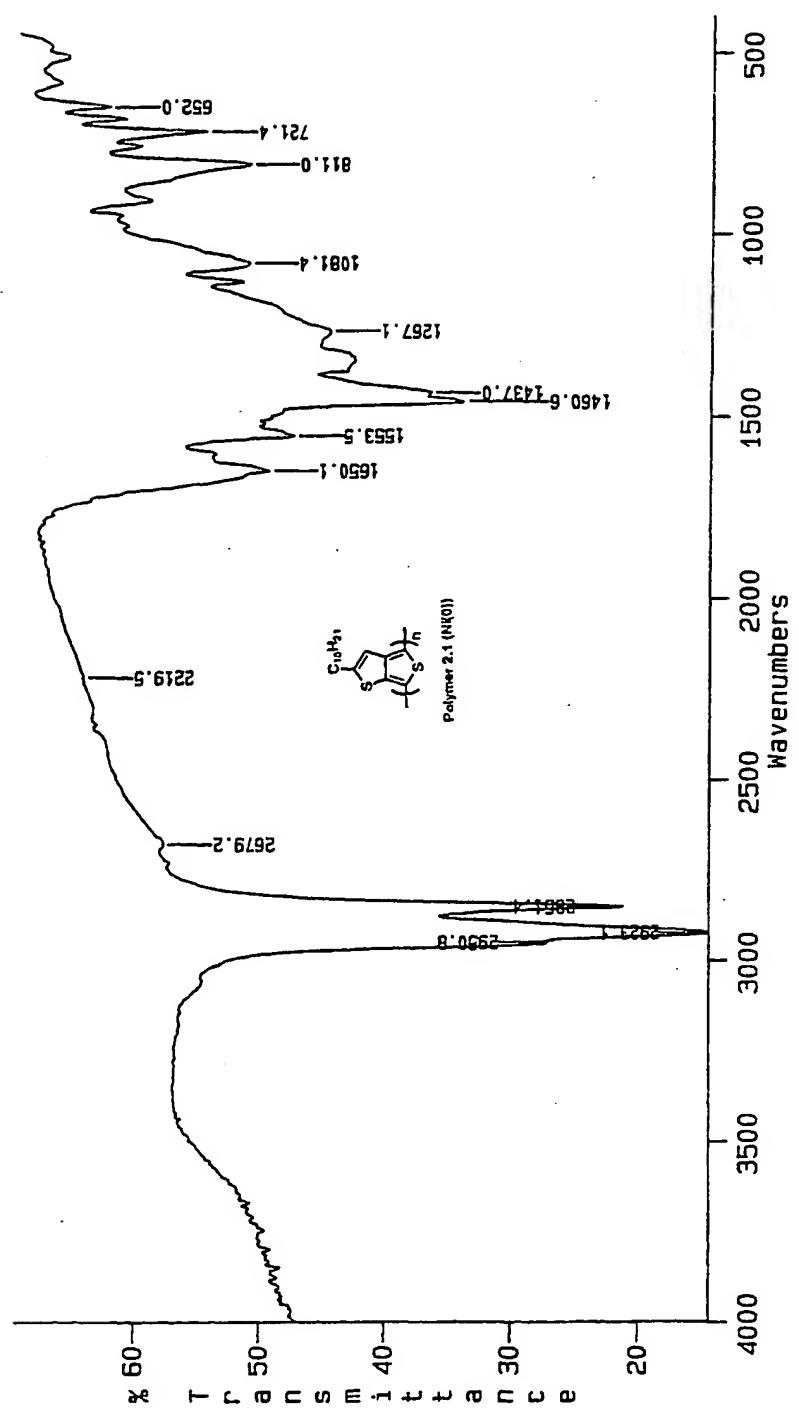






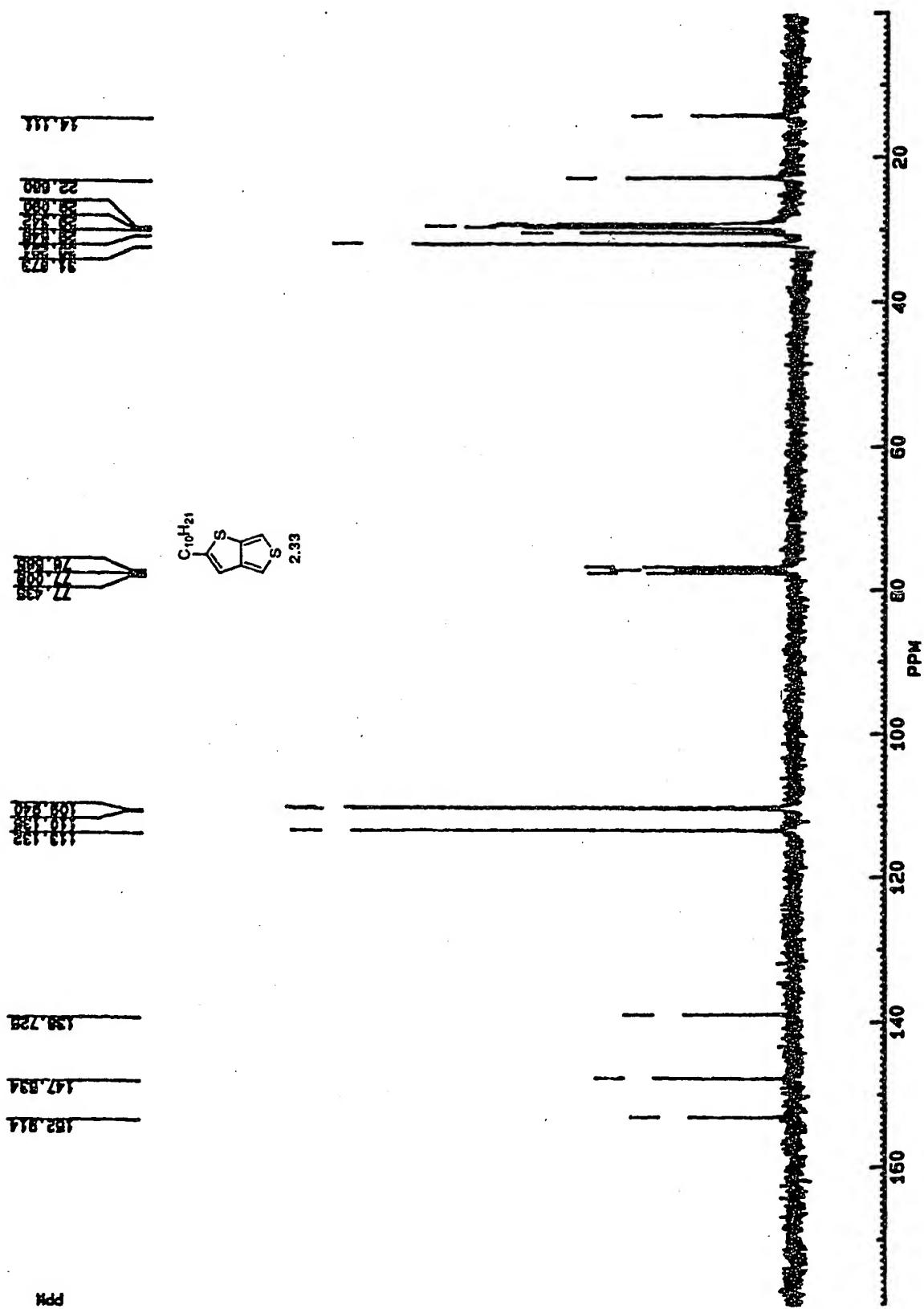
APPENDIX III
¹H NMR AND IR SPECTRA OF POLYMER 2.1
FROM NICKLE(0) COUPLING

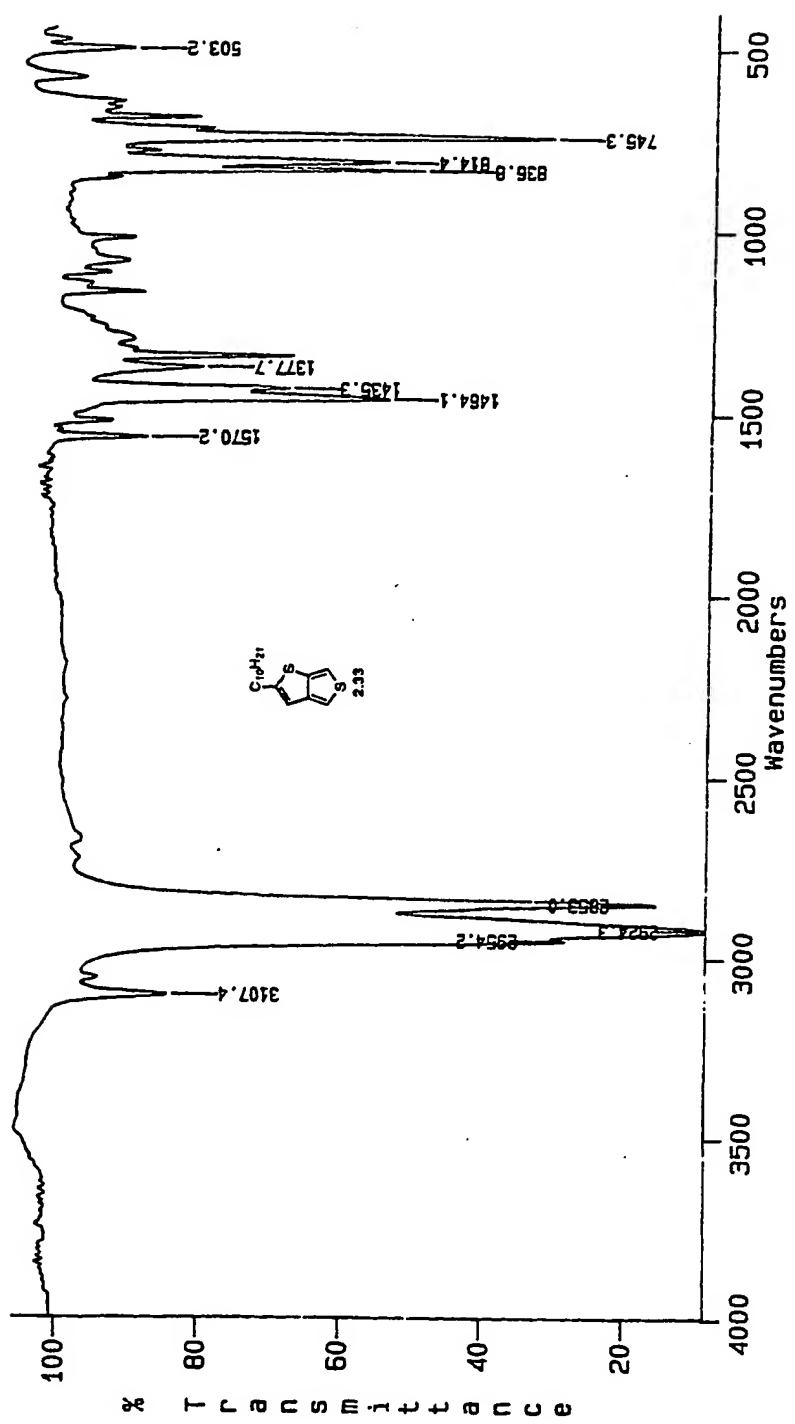




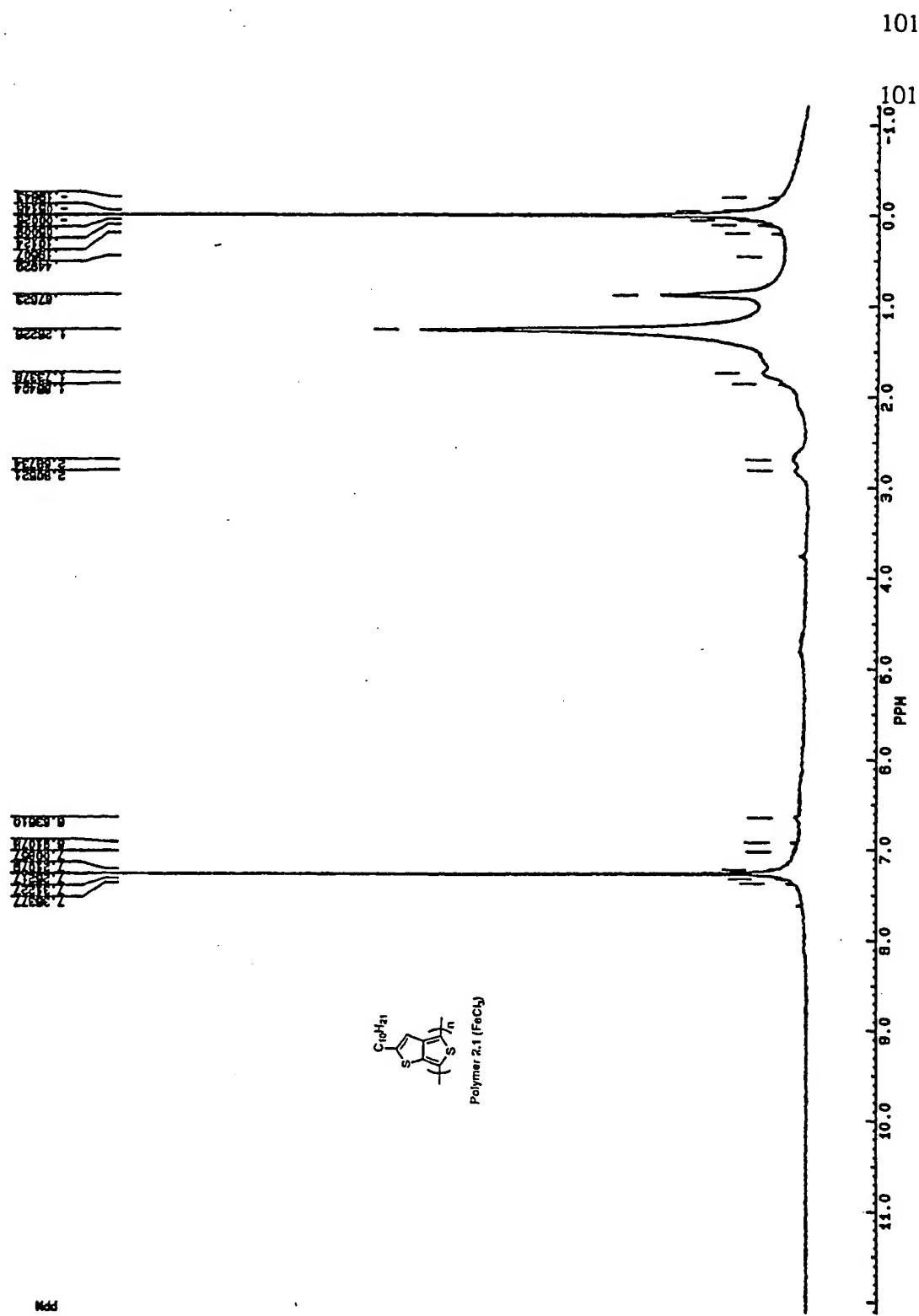
APPENDIX IV

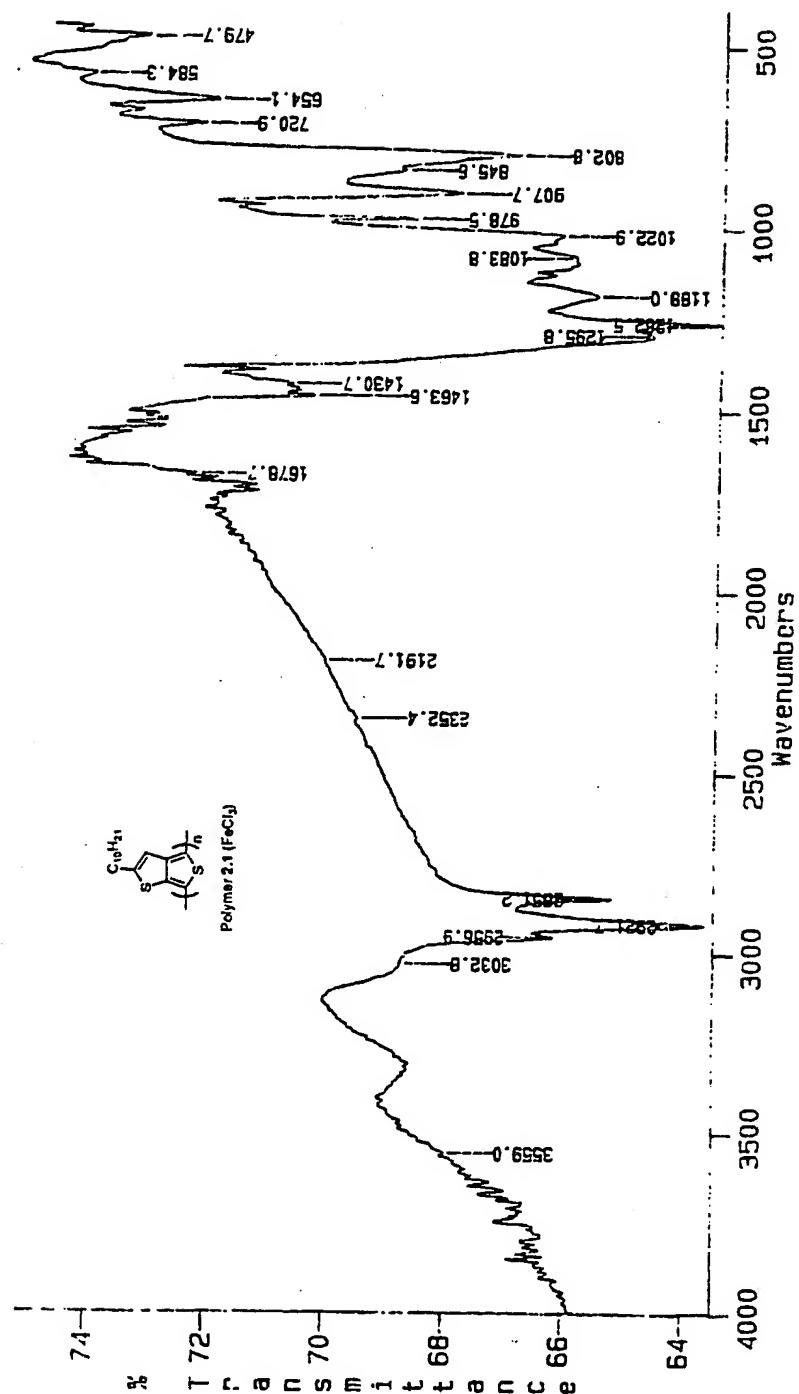
^1H NMR, ^{13}C NMR AND IR SPECTRA OF 2-DECYL-
THIENO[3,4-b]THIOPHENE (2.33)





APPENDIX V
¹H NMR, IR AND UV-VIS SPECTRA OF POLYMER 2.1
FROM FERRIC CHLORIDE





103

NM

1440.00

960.00

720.00

480.00

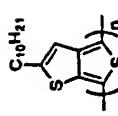
0.1000

0.2000

0.3000

ABS

Polymer 2.1 lilm (FeCl₃)



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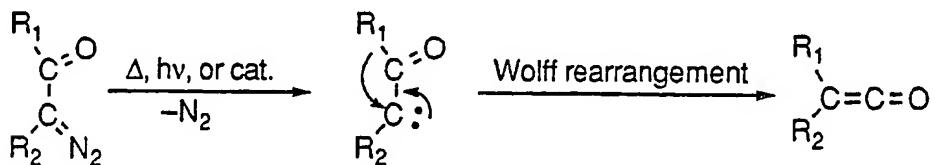
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**PART II: FORMATION AND TRAPPING OF
METHOXY(METHOXY-
CARBONYL)KETENE**

INTRODUCTION

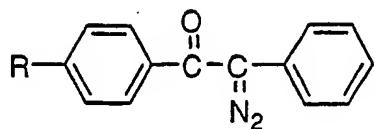
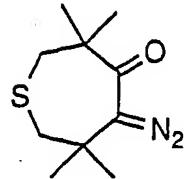
It is well known that α -diazo carbonyl compounds can rearrange to the corresponding ketenes under certain conditions.^{1,2} The rearrangement, which involves the loss of N₂ to produce the carbene, followed by formation of the corresponding ketenes (Scheme I), received much attention in mechanistic study in the earlier years.^{1,3} This specific rearrangement is known as the Wolff rearrangement after its discoverer.⁴ The rearrangement can be induced by thermolysis,⁵ photolysis⁶ or catalysis (Lewis acid).⁷ The thermolysis occurs over a wide range of temperatures depending on the reactivity of the diazo compounds (room temperature to 750 °C).

Scheme I

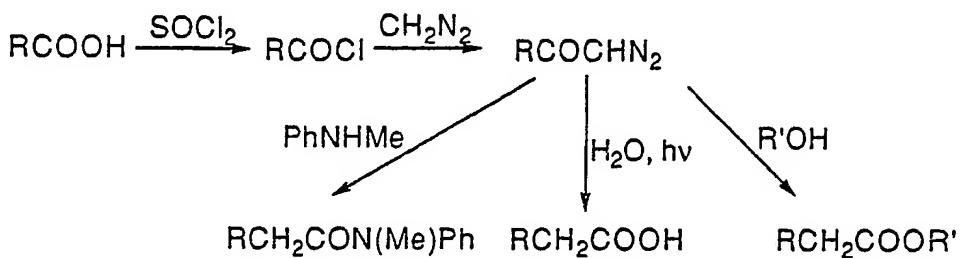


Stability of the α -diazo carbonyl compounds is mainly a function of electronic effects. The substituents could cause changes to the electron density of the α -diazo carbonyl unit and thus influence the stability of the compounds. Thermal stability of the α -diazo carbonyl compounds decreases with increasing electron-accepting character of the acyl group. A good example is that substituted azibenzils (1) with electron-accepting groups R increase the decomposition rate of the α -diazo carbonyl compounds, while electron-donating groups have the opposite effects. The substituents can also cause a twisting of the carbon-carbon bond which reduces the extent of overlap between the C=O and C=N₂ groups and lowers the

stability.¹ The ring strain of compound **2** is responsible for the decomposition of **2** at room temperature.

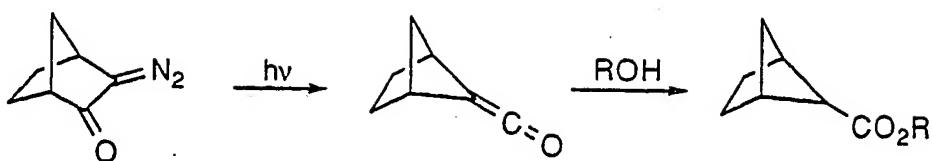
**1****2**

The Wolff rearrangement is very useful in organic synthesis.³ For example, it can be used for chain lengthening. The synthesis usually proceeds via the Arndt-Eistert synthesis where an acid chloride reacts with an excess of diazoalkane to form an α -diazoketone. The second step is a Wolff rearrangement of the α -diazoketone. The rearrangement products, ketenes, can react with nucleophiles such as water, alcohols and amines to yield carboxylic acid, ester and amide (Scheme II).

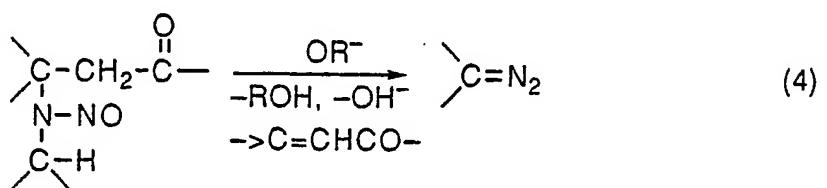
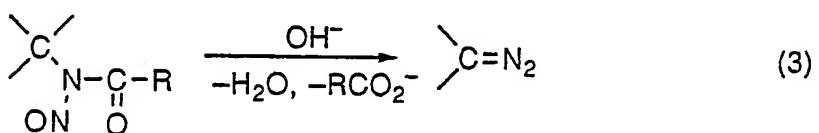
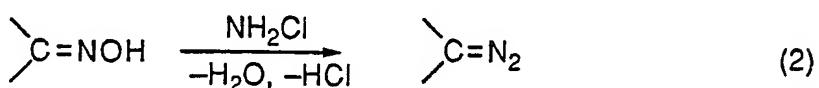
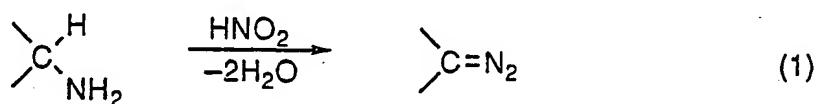
Scheme II

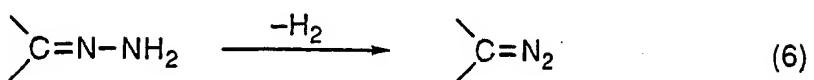
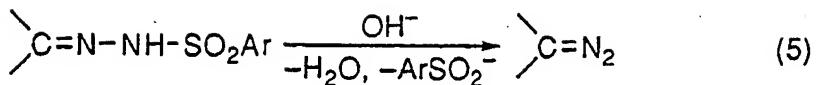
Wolff rearrangement of cyclic α -diazoketones can also be used to contract a larger ring to a smaller strained ring (3-4 membered ring) compound which could be very difficult to make by other methods (Scheme III).^{8,9}

Scheme III

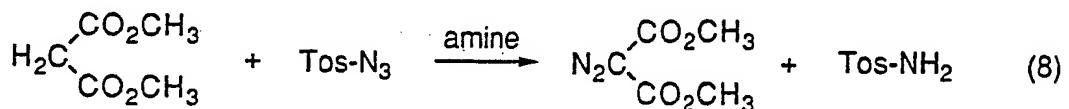


There are several ways to synthesize α -diazo carbonyl compounds,¹⁰⁻¹³ e. g. by diazotization of an amine (equation 1); by the Forster reaction (equation 2); by deacylation of the *N*-acyl-*N*-nitrosoalkylamines (equation 3); by alkaline cleavage of β -(*N*-alkyl-*N*-nitrosoamino)ketones (equation 4); by the Bamford-Stevens reaction, cleavage of arenesulfonyl hydrazones (equation 5); by dehydrogenation of hydrazones (equation 6) and by direct diazo group transfer reaction (equation 7)¹⁴ and so on.





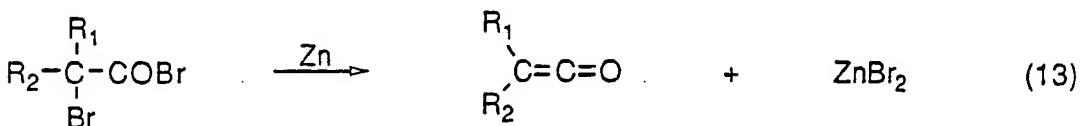
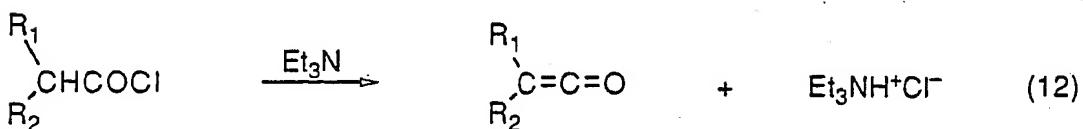
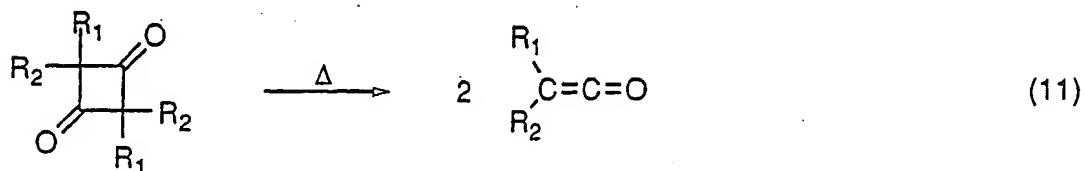
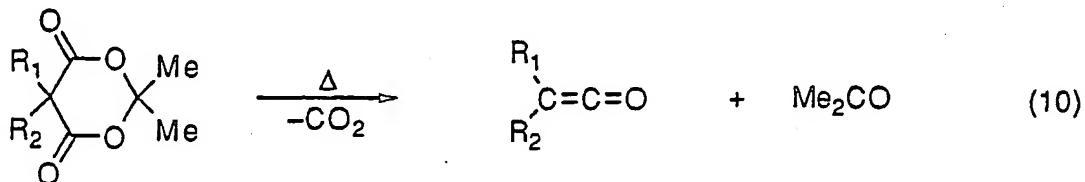
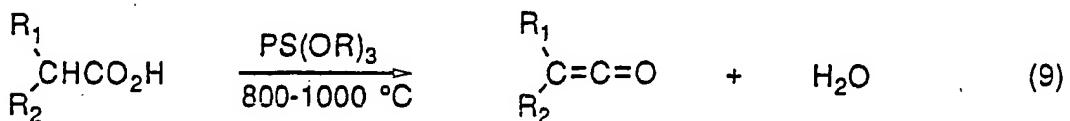
In the diazo group transfer method, the entire N₂ group is transferred to a target molecule from a donor molecule by either exchange or addition. Sulfonyl azides, especially tosyl azide, are a good choice for diazo transfer reagents. Tosyl azide can be easily prepared by chloride-azide exchange. Equation 8 shows the diazo group transfer from tosyl azide to dimethyl malonate.¹⁰



Ketenes have found wide interest among organic chemists over the years. Ketenes have been extensively studied and frequently reviewed because of their interesting organic functional group.¹⁵⁻¹⁹ The first reported ketene was synthesized by Hermann Staudinger in 1905.²⁰ It has become a research area of interest again recently^{21,22} and, as mentioned by Tidwell, the recent years are "The second golden age" of ketenes.²¹

Ketenes are usually very reactive species. In fact these species are so unstable that very few ketenes can be isolated at room temperature. Ketene itself rapidly forms its dimer. This dimer can serve as a laboratory precursor for monomeric ketene as will be mentioned later. Because of the difficulty of isolating ketenes, they are sometimes studied by trapping with alkenes. Ketenes can also be directly studied at low temperature.²³

Ketenes can be generated in several different ways. In addition to Wolff rearrangement of diazocarbonyl compounds, general methods of preparing ketenes include high temperature decomposition of carboxylic acids, anhydrides, ketones, and esters (equation 9); decomposition of malonic acid derivatives (equation 10); regeneration from the dimers (equation 11); dehydrohalogenation of acyl halides (equation 12) and dehalogenation of α -haloacyl halides (equation 13) and so on.^{17,18,22}



The stability of the ketenes is affected by the stereochemical properties and the electronic properties of substituents (R_1, R_2).²⁴ The bulkier the substituent groups the lower

are the reactivities.¹⁷ Electropositive substituents stabilize ketenes and electronegative substituents destabilize ketenes. Evidence also shows that π electron acceptor substituents stabilize ketenes and π electron donor substituents destabilize ketenes. For example acylketenes are more stable because the acyl group acts as a π acceptor and stabilizes the ketene (Figure 1). Alkoxyketenes are less stable because of the high electronegativity and the $n-\pi$ repulsion involving the oxygen lone pair.

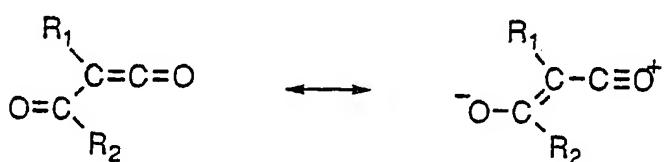


Figure 1. Resonance structure of acyl ketenes

Theoretical studies of ketenes show that the oxygen and β carbon on ketenes carry a partial negative charge and the α carbon has a partial positive charge density (Figure 2 shows the charge density for ketene).²¹ The NMR spectra of ketenes show a low field value for the α carbon (typical carbonyl range) and a very high field value for the β carbon ($\delta = 2.5$ ppm for ketene itself, varies depending on the substituents), which agree with the theoretical studies.

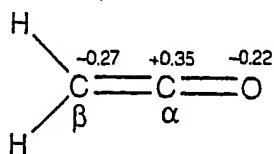
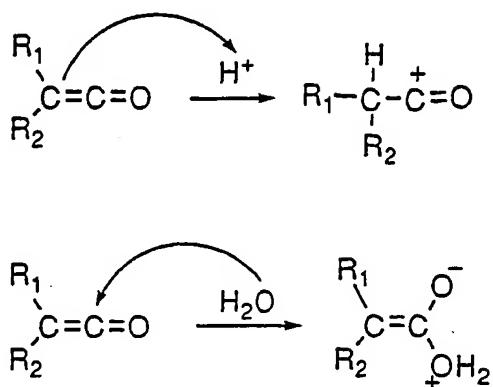


Figure 2. Ketene charge density

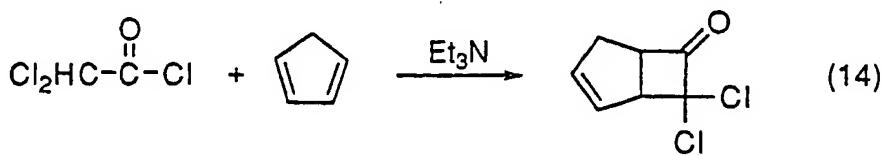
The charge distribution in ketenes shows that the oxygen and β carbon are susceptible to attack by electrophiles and electrophilic attack usually occurs in the plane perpendicular to the ketene, while nucleophiles will usually attack the α carbon and nucleophilic attack usually

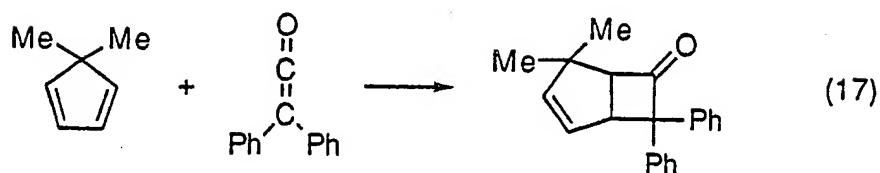
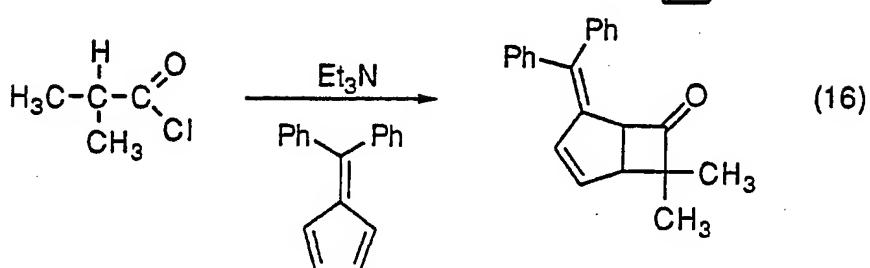
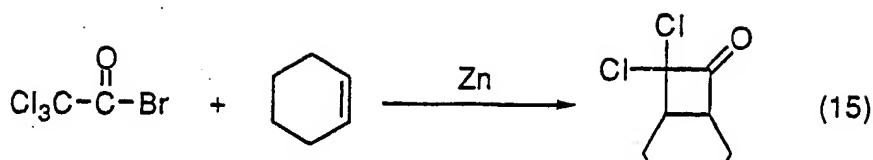
occurs in the ketene plane. Acid-catalyzed hydrolysis and neutral hydrolysis of ketenes are good examples as shown in Scheme IV.²¹

Scheme IV



Besides nucleophilic and electrophilic addition reactions, ketenes can undergo [2+2] cycloaddition with a variety of alkenes to form substituted cyclobutanones. The cycloaddition of ketenes with cyclic alkenes will form bicyclic compounds which are important intermediates in a wide variety of synthetic reactions. These cyclic alkenes include cyclopentadiene (equation 14),²⁵ cyclohexene (equation 15),²⁶ dimethylfulvene (equation 16),²⁷ 1,1-dimethyl cyclopentadiene (equation 17)²⁸ another molecule of the ketene itself²⁹ and so on.





The cycloaddition of ketenes with alkenes and dienes has attracted significant theoretical interest. Though massive research has been done on the reaction mechanism of the cycloaddition of ketenes with alkenes and dienes, the mechanism still remains unclear. The reaction mechanism was studied extensively in the 1970's. Cycloaddition of ketenes with alkenes to form cyclobutanones is one of the characteristic ketene reactions. It is well known that the reaction of ketene and an alkene always produces the [2+2] cis addition product. Even when a ketene reacts with dienes it still forms a cyclobutanone and no Diels-Alder products are produced (ketene can not act as a dienophile). Furthermore, the adducts from unsymmetrical ketenes and cyclic alkenes usually give a product with the larger substituent in the endo position, which is seemingly sterically more hindered. Extension of the Woodward and Hoffmann pericyclic reaction selection rules suggested that the cycloaddition occurs by a concerted ($\pi^2_s + \pi^2_a$) path in which the ketene plays an antarafacial role and the alkene plays a suprafacial role.^{30,31} The reactants approach in an orthogonal way. Cycloaddition of

monosubstituted ketenes and cyclopentadiene often produces endo-7-substituted bicyclo[3.2.0]hept-2-en-6-one. As shown in Figure 3, ketene and cyclopentadiene approach in an orthogonal way and the transition state will lead to an isomer with the larger group (L) at the endo position and smaller group (S) at the exo position.

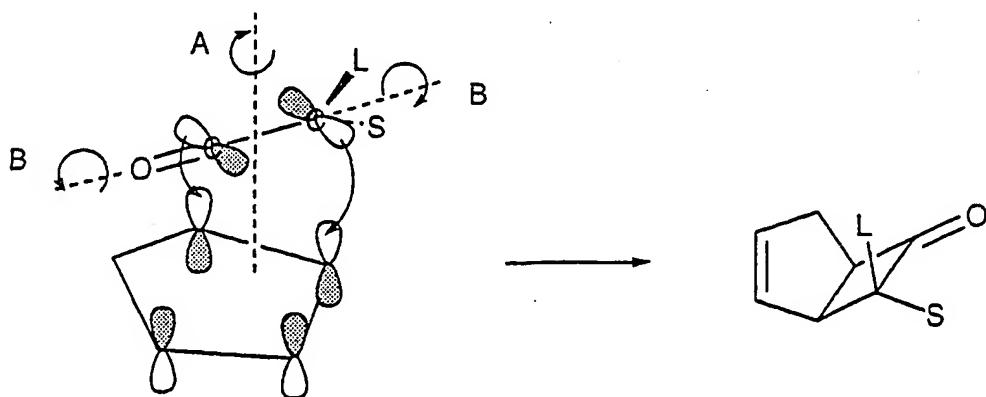
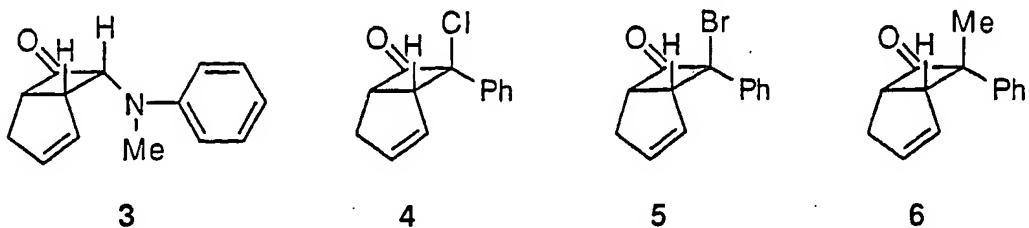


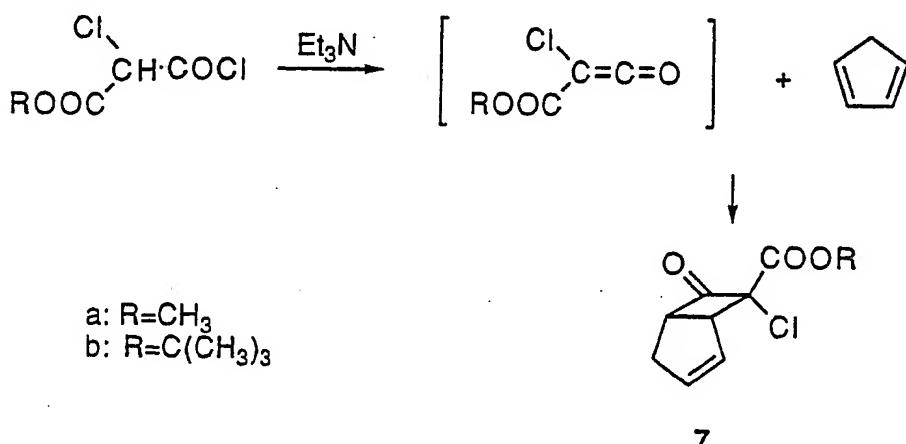
Figure 3. Stereochemistry of ketene and cyclopentadiene adducts

Even though there were some exceptions, most of the known reactions between ketenes and cyclopentadiene showed stereochemistry consistent with Woodward and Hoffmann's prediction. For example, the aminoketene-cyclopentadiene adduct 3, the phenylchloroketene-cyclopentadiene adduct 4, the phenylbromoketene-cyclopentadiene adduct 5 and the phenylmethylketene-cyclopentadiene adduct 6 are all in agreement with Woodward and Hoffmann's prediction.



There are some exceptions concerning the stereochemistry of the adducts. Goldstein et al., reported the synthesis of 7-chloro-7-alkoxycarbonylcyclo[3.2.0]hept-2-en-6-one (**7a** and **7b**) in 1981 (Scheme V).³² An X-ray crystal structure of the products **7a** and **7b** indicated chlorine was in the endo and alkyl ester group in the exo position, which disagreed with the Woodward-Hoffmann prediction because chlorine is a smaller group than the ester groups.³¹ The explanation proposed by Goldstein et al.,³² was that in the transition state "steric repulsion could be largely compensated for by a stabilizing interaction between the electron-enriched ester group and the electron-deficient end of the reacting carbon-carbon double bond".³²

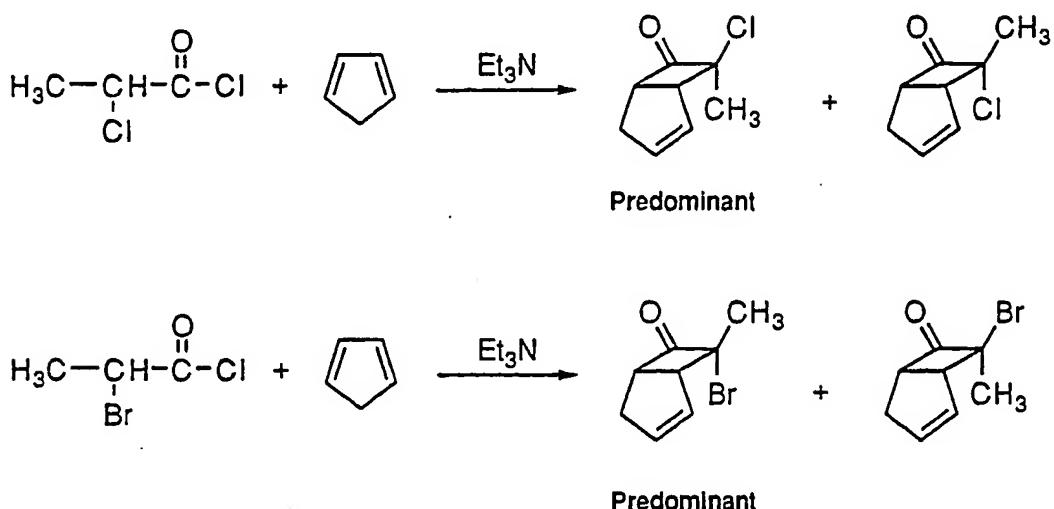
Scheme V



Brady also reported in 1970 that there is a reversal in the endo- and exo-methyl adduct isomers which are derived from the reactions of $\text{H}_3\text{CC}(\text{Br})=\text{C}=\text{O}$ and $\text{H}_3\text{CC}(\text{Cl})=\text{C}=\text{O}$ with cyclopentadiene.³³ The exo-methyl isomer is the predominant adduct for the $\text{H}_3\text{CC}(\text{Br})=\text{C}=\text{O}$

and cyclopentadiene reaction and the endo-methyl isomer is the predominant adduct for the H₃CC(Cl)=C=O and cyclopentadiene reaction (Scheme VI).

Scheme VI



The simple picture for the cycloaddition of ketenes and alkenes provided by the Woodward-Hoffmann rules was challenged by other theoretical chemists.³⁴⁻⁴² One major question was whether the reactions are concerted or stepwise. Even in 1970 there were extensive speculations that instead of a synchronous concerted cycloaddition as proposed by Woodward-Hoffmann, the reaction might be a two step reaction. Their argument was that ketenes are highly polar molecules. They are expected to have polar character in the reaction transition states. Instead of a ($\pi^2_s + \pi^2_a$) pathway, it is thought that the process may be better described as a [$\pi^2_s + (\pi^2_s + \pi^2_s)$] pathway. In the [$\pi^2_s + (\pi^2_s + \pi^2_s)$] process, the more nucleophilic carbon of the alkene first attaches to the C_α atom of the ketene, then the other carbon atom of the alkene electrophilically attaches to the C_β atom of the ketene and completes the ring closure (Figure 4).³⁶

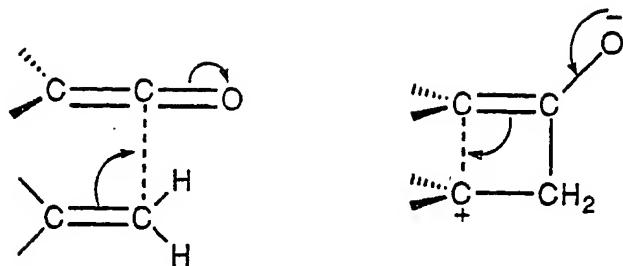


Figure 4. Electron movement in $[\pi 2_s + (\pi 2_s + \pi 2_s)]$ mechanism

There is a tremendous amount of recent theoretical studies on the cycloaddition of ketenes to alkenes.³⁷⁻⁴³ Bernardi et al., used ab initio MCSCF computational methods to analyze the reaction between an ethylene and ketene.⁴² Two mechanisms were suggested by them and were called C1(II) approach and C1(\perp) approach. In the C1(II) approach, the formation of the first carbon-carbon bond involves one ethylene carbon atom and the C1-ketene carbon (Figure 5). The attack occurs in the ketene molecular plane (parallel approach). The diradical intermediate, if it exists, is very short lived. The ring closure gives a cyclobutanone. According to their computational results, the C1(II) approach is not a two step mechanism; it is rather a "concerted, nonsynchronous two stage mechanism".⁴² Since this reaction mechanism is concerted in nature, the stereoselectivity is preserved. The C1(\perp) approach is a two step reaction mechanism. In this reaction mechanism, the formation of the first carbon-carbon bond still involves one ethylene carbon atom and the C1-ketene carbon, but the attack happens in the plane orthogonal (perpendicular) to the ketene molecule (Figure 5). The intermediate is diradical in nature with the two unpaired electrons located mainly on the other ethylene carbon and on the oxygen atom of the ketene. This mechanism is a two step nonconcerted pathway and will lead to a loss of stereospecificity. The reaction product of C1(\perp) approach is also a cyclobutanone.

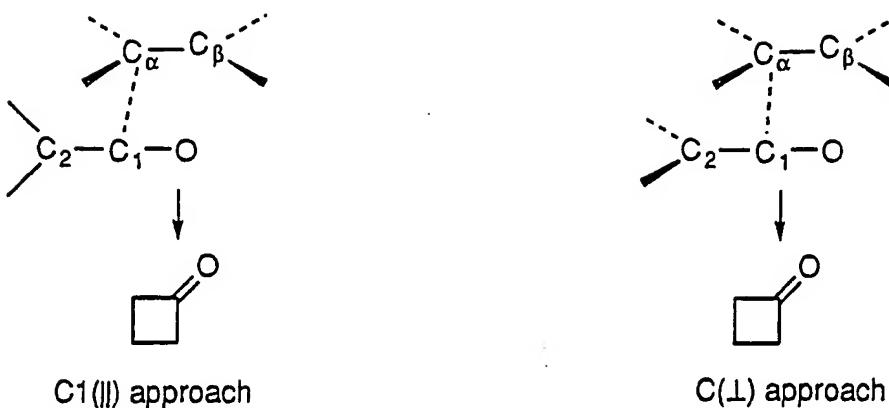


Figure 5. Schematic representation of $\text{C}_1(\text{II})$ approach and $\text{C}_1(\perp)$ approach

The cycloaddition of ketene and ethylene was also studied by Wang et al.,⁴⁰ at the MP2 / 6-31G * level. The central carbon of the ketene (C_1) interacts strongly with both carbons of the ethylene molecule (C_α and C_β). In the transition state the forming bond between the central ketene carbon C_1 and one ethylene carbon C_α is 1.78 Å, the other forming bond, between C_2 of the ketene and C_β of the ethylene, is 2.43 Å, much longer than the first one.⁴⁰ Instead of forming a diradical intermediate, they suggested that there was considerable charge separation in the transition state with C_β of the ethylene becoming more positively charged and oxygen of the ketene becoming more negatively charged.

Regioselectivity is another characteristic of the ketene and cyclopentadiene addition. The products are always bicyclo[3.2.0]hept-2-en-6-ones and not bicyclo[3.2.0]hept-2-en-7-ones. Perturbation theory predicts that bonding occurs between the C_1 of the ketene, the atom with the highest coefficient in the LUMO, and the carbon of the alkene with the highest coefficient in the HOMO. Bonding between these two carbons produces the most stabilized zwitterionic intermediate (Figure 6).¹⁹

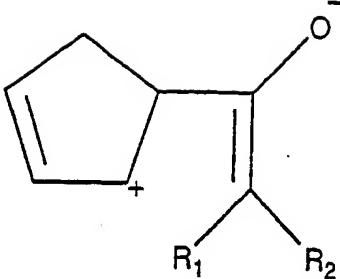


Figure 6. Zwitterionic intermediate for the cycloaddition of ketenes and cyclopentadiene

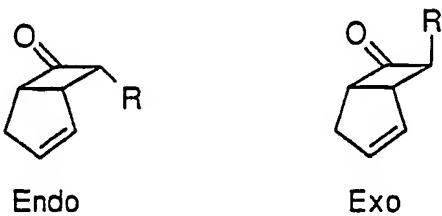
The stereochemistry of ketenes and cyclopentadiene adducts have been studied extensively over the years. The structures of the reaction products were studied by NMR spectroscopy^{44,45} and X-ray crystallography.^{46,47} NMR spectroscopy was used to determine the structure using the fact that proton coupling constants are different between the cis- and trans-adducts. While NMR spectroscopy frequently provides insufficient information about the structure, X-ray crystallography can usually be used to determine the whole molecular structure including stereochemistry. For example, the structure of 7a and 7b were both determined by X-ray crystallographic methods.

Reports on the stability of endo- versus exo-isomer of 7-monosubstituted bicyclo[3.2.0]hept-2-en-6-one were contradictory. Most of the reports say the exo-isomer is the more stable compound, which agrees with intuition. Brady reported in 1970 that the endo-isomer can be equilibrated to the exo-isomer in solution (e.g. Et₃N).⁴⁸ But Rey et al., reported exactly the opposite; the endo-isomer is the more stable product.⁴⁹ They demonstrated the equilibration of the two isomers, and the ratios of the two isomers are shown in Table 1.

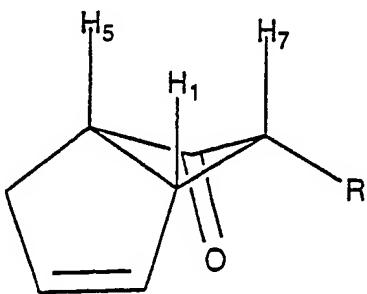
Except for the case involving the *t*-Bu substituent, the endo-isomers were preferred. The ratio of endo- and exo-isomers was determined by NMR spectroscopy. It was concluded that the cyclobutanone ring was not planar. Instead it has a rather puckered structure with the

Table 1. The Isomer Ratio at Equilibrium for 7-Monosubstituted**Bicyclo[3.2.0]hept-2-en-6-one**

R	Endo	Exo
F	88.7	11.3
Cl	86.7	13.3
CH ₃	76.3	23.7
Et	64.4	35.6
i-Pr	56.9	43.1
t-Bu	9.6	90.4
Ph	67	33



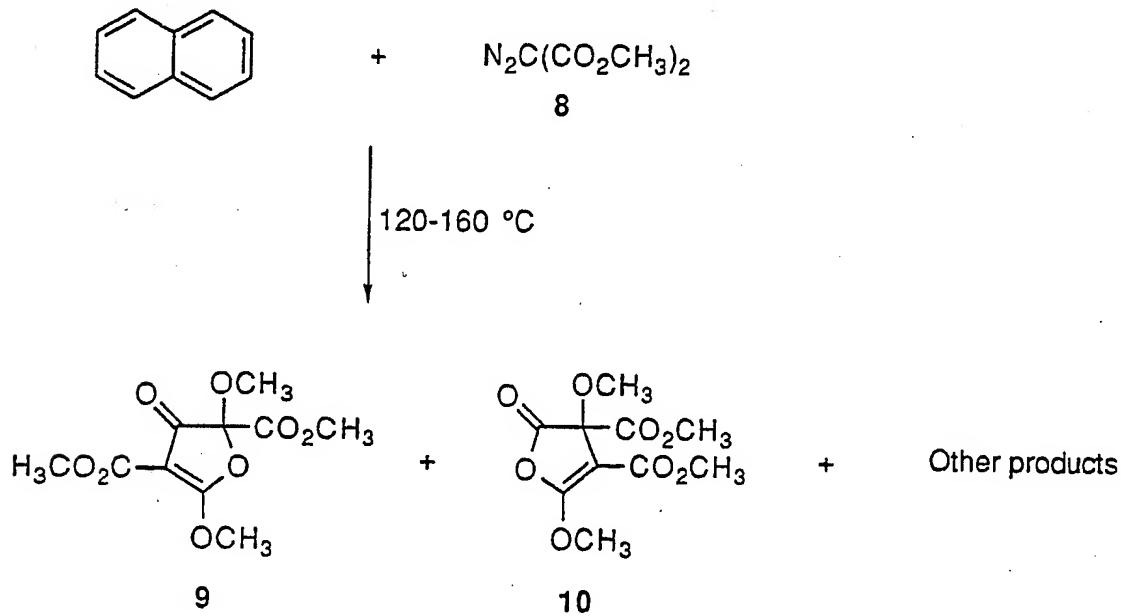
carbonyl group turned toward the endo-side (Figure 7). This puckered structure could possibly have a favorable electronic interaction between H₅ and the carbonyl group with the H₅-C bond lying orthogonal to the carbonyl group. The endo-isomer is more crowded, but this is offset by the preference of H₇ for the exo-position, so as to be orthogonal to the carbonyl plane.

**Figure 7.** Puckered endo-isomer of 7-monosubstituted bicyclo[3.2.0]hept-2-en-6-one

RESULTS AND DISCUSSION

It was observed several years ago that in the thermal reaction of dimethyl diazomalonate (8) with naphthalene, two dimers, dimer 9, a dihydrofuranone, and dimer 10, a butenolide, were formed in 30% yield (ratio 1:5) in addition to the other products (Scheme VII).²

Scheme VII



The yield and ratio of the two dimers produced in the thermal decomposition of the diazo compound 8 have been studied as a function of the reactant / solvent (5 : 1 ratio of the reactant / solvent : dimethyl diazomalonate / 140 °C / 5 hours). The results are shown in Table 2. As has been pointed out, when naphthalene is used as the reactant / solvent, the ratio of 9 to 10 is 5 : 1 with 9 as the major product. With *p*-dichlorobenzene and chlorobenzene, the 9 : 10

ratio is 7 : 1 and 6.5 : 1 respectively. However, with 1-chloronaphthalene the ratio is reversed to 1 : 1.8 (Table 2).

Table 2. Ratio of 9 : 10 and Yield*

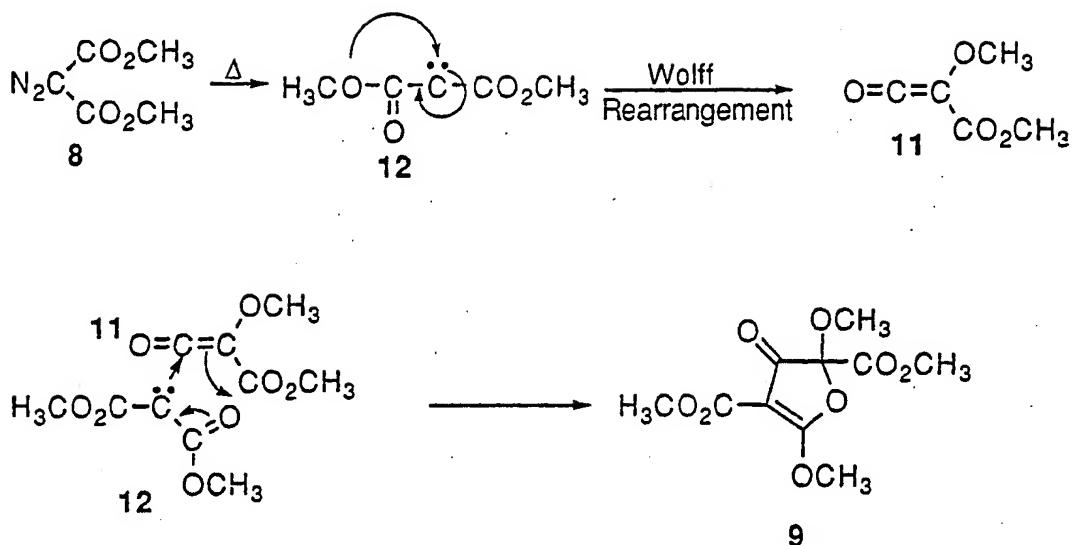
Solvent/Reactant	9	10	Approx. Yield (%)
Naphthalene	5	1	30
Anthracene	-	only	20
Phenanthrene	-	only	10
Benzene	-	-	-
2,3-Dimethylnaphthalene	only	-	<3
<i>p</i> -Xylene	-	-	-
<i>p</i> -Dichlorobenzene	7	1	50
Chlorobenzene	6.5	1	30
1-Chloronaphthalene	1	1.8	30
Bromobenzene	1	1	50
<i>p</i> -Dimethoxybenzene	-	-	-
CH ₂ I ₂	-	-	-
Neat	-	only	20

* Results from Dr. M. Pomerantz and Dr. M. Levanon⁵²

The mechanism for formation of dimer 9 and dimer 10 under these thermal conditions was not very clear. However, it is very possible that the reaction involves the Wolff rearrangement of the diazo compound 8 to the corresponding ketene. Yet a previous report⁵⁰ shows that, the lowest temperature at which this rearrangement would occur in gas phase was 280 °C, but the reaction temperature here is 160 °C lower.

Dimer 9 was previously obtained by Regitz and Maas⁵¹ upon photochemical decomposition of 8 in molten *p*-dichlorobenzene. They did not observe dimer 10 though they were expecting to. They postulated that bis(methoxycarbonyl)carbene (12), which is generated from the diazo compound 8, underwent a photochemical Wolff rearrangement to form the corresponding ketene, methoxy(methoxycarbonyl)ketene (11), followed by a [3+2]-cycloaddition of another carbene 12 to the resulting ketene 11 (Scheme VIII).

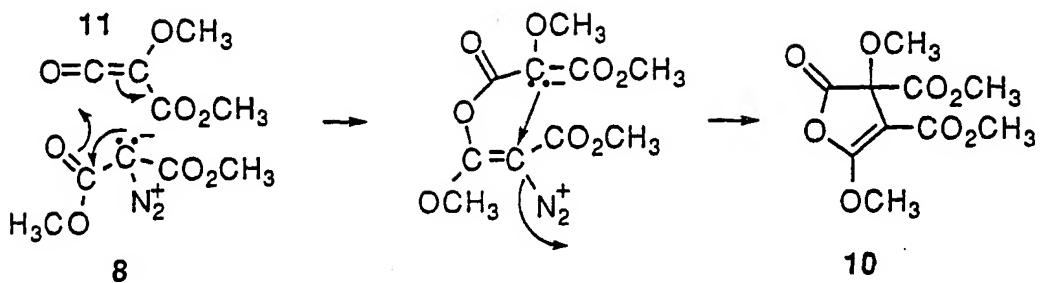
Scheme VIII



After the observation of the formation of dimer 9 and dimer 10 under the reaction conditions listed in Table 2, Dr. Pomerantz and Dr. Levanon postulated the reaction mechanism for the formation of the two dimers. Because of the strange variation in product ratios with solvent/reactant shown in Table 2 it was suggested that dimer 9 and dimer 10 were formed by two different reaction pathways. Dimer 9 seemed to be formed by [3+2]-cycloaddition of the carbene 12 to the ketene 11 as shown in Scheme VIII. Dimer 10 possibly came from the reaction of the diazo compound 8 with the ketene 11 (Scheme IX).⁵² Lactone products have been shown to arise by direct reaction of ketenes with diazo compounds under conditions where the diazo compounds do not form carbenes.^{53,54} Thus it was reasonable to assume that 10 is formed from the diazo compound and 9 from the carbene.

In an attempt to provide evidence for these mechanisms, ketene 11 was generated independently in the presence of the dimethyl diazomalonate 8 under conditions where 8 would not lose N_2 to give the carbene 12. It was hoped that dimer 10 might be formed and not dimer 9 which would provide evidence for the proposed mechanism. The synthesis followed the

Scheme IX



traditional route, the dehydrochlorination of methyl 3-chloro-2-methoxy-3-oxopropanoate (13) by triethylamine. The ketene 11 was generated in the presence of the diazo compound 8 under several different reaction conditions. These conditions were selected, as indicated above, so that the diazo compound 8 would not decompose. If one or both dimers were observed in these reaction conditions, then the dimers are from the reaction between diazo compound 8 and the ketene 11, not from the ketene 11 and the carbene 12. The reactions were monitored by gas chromatography (GC retention time 13.5 min. for 9 and 11.7 min. for 10).

All the reaction conditions are described in the experimental section. They varied from temperatures as low as -78°C to boiling toluene (110°C) in a number of different solvents. Reaction conditions 1-3 used benzene as reaction solvents, and the reaction temperatures were varied from 0°C to reflux (80°C). Reaction conditions 4 and 5 used CH_2Cl_2 as reaction solvents; temperatures varied from -78°C to 0°C . Reaction conditions 6 and 7 used THF as reaction solvents; temperatures varied from -78°C to 0°C . Reaction conditions 8 and 9 used ethyl ether as reaction solvents; temperatures varied from -78°C to 0°C . Reaction conditions 10 and 11 used toluene as reaction solvents; temperatures varied from room temperature to reflux.

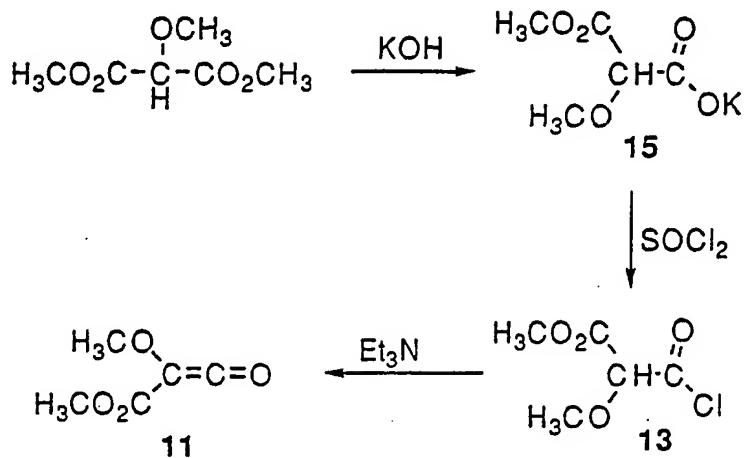
Neither of the dimers **9** or **10** were detected by GC or NMR spectroscopy among the reaction products from any of the reactions attempted. Under the reaction conditions 1-10, no GC peaks of dimer **9** or dimer **10** were observed. In experiment 11, using refluxing toluene as solvent, peaks near retention times (Appendix VI shows the GC chromatogram) of dimer **9** and dimer **10** were observed, but the ^{13}C NMR spectrum showed no characteristic peaks for dimer **9** or dimer **10** at 106.4 ppm (carbon-carbon double bond peak for compound **9**) or 99.4 ppm (carbon-carbon double bond peak for compound **10**). In all cases dimethyl diazomalonate (**8**) was recovered.

Dimethyl diazomalonate (**8**) was synthesized according to the literature procedure in 90% yield.⁵⁵ The diazo group was transferred to dimethyl malonate from tosyl azide in the presence of triethyl amine. The ^1H NMR spectrum showed a singlet at 3.85 ppm (literature⁵⁶ 3.80 ppm in CCl_4) for the methyl peak of the ester group. The ^{13}C NMR spectrum showed the carbonyl peak at 161.3 ppm, the CN_2 peak at 65.5 ppm and the methyl peak of ester group at 52.4 ppm.

Scheme X shows the synthetic route to methoxy(methoxycarbonyl)ketene (**11**). Methyl 3-chloro-2-methoxy-3-oxopropanoate (**13**) was made according to a procedure obtained from the literature¹¹ with a slight modification. Methanol was used instead of ethanol to prevent possible ester exchange. Potassium hydroxide solution in methanol was dropped into a dimethyl methoxymalonate solution in methanol at room temperature. The addition of the potassium hydroxide was slow in order to prevent the di-hydrolysis of the dimethyl methoxymalonate. Rapid addition of potassium hydroxide could cause the formation of a precipitate which is an indication of the di-hydrolysis of dimethyl methoxymalonate. The NMR spectrum of the filtered solid confirmed the presence of the di-hydrolysis product. The concentration of dimethyl methoxymalonate solution in methanol should also be kept very

dilute for the same reason. After drying, the resulting hydrolysis product can be used directly to make the acid chloride in the next step.

Scheme X



The ^1H NMR spectral data of the di-hydrolysis product **14** (structure shown in Table 4), the half hydrolysis product **15** and the acid chloride **13** are shown in Table 3. The ^{13}C NMR chemical shifts of the di-hydrolysis product **14**, the half hydrolysis product **15** and the acid chloride **13** are shown in Table 4.

Table 3. Proton Chemical Shifts of Compounds 13, 14 and 15*

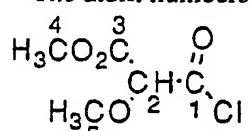
Compounds	Chemical Shift (δ , ppm)			
	H2	H3	H4	H5
13	4.67		3.88	3.58
14	3.91	3.16		
15	4.25		3.66	3.26

* See footnote of Table 4.

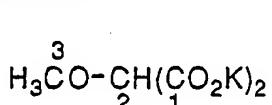
Table 4. ^{13}C Chemical Shift of Compounds 13, 14 and 15*

compounds	Chemical Shift (δ , ppm)				
	C1	C2	C3	C4**	C5**
13	164.9	86.6	168.9	53.5	59.1
14	178.0	87.8	59.1		
15	173.7	84.9	174.7	55.5	59.9

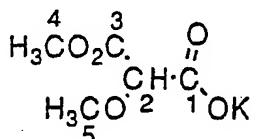
* The atom numbers are as follows:



13



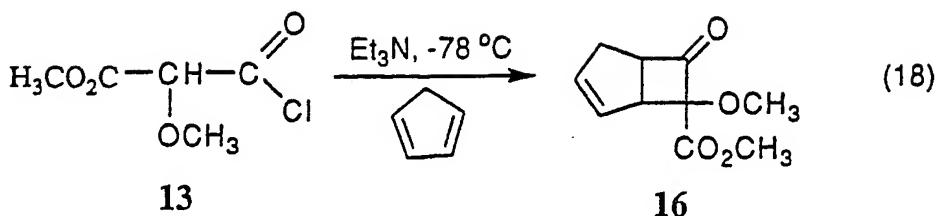
14



15

** Assignment based on the fact that carboxylate anion carbons usually have lower chemical shifts than ester carbons.⁵⁷

Methoxy(methoxycarbonyl)ketene (11) was generated from the acid chloride by dehydrochlorination with triethylamine¹⁷ and, as discussed above, was allowed to react with dimethyl diazomalonate in situ. Neither of the dimers 9 and 10 were detected. One possibility was that dimers 9 + 10 were not formed because the ketene was not generated. The second possibility is that the ketene was formed but it did not react with the dimethyl diazomalonate (8) under the conditions used. To prove that the ketene 11 was indeed produced it was generated in the presence of a trapping agent, cyclopentadiene. Equation 18 shows the expected pathway if the ketene 11 is produced from 13 and reacts with cyclopentadiene.¹¹ Cyclopentadiene was chosen as a trapping agent because it can trap very reactive ketenes, it usually reacts with ketene in a [2+2] sense and the ketene precursor can not react with it. The formation of the compound 16, 7-methoxy-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one, is an indication of the presence of the ketene 11.



Methoxy(methoxycarbonyl)ketene has an electron withdrawing ester group and an electron donating methoxy group. Acylketenes are of considerable current interest not only because of theoretical stereochemical studies but also they are versatile intermediates in organic synthesis.^{21,58} Ketenes bearing electron donating groups show an increased reactivity in cycloaddition reactions, and ketenes bearing electron withdrawing groups show decreased reactivity. While ketenes bearing electron donating groups or electron withdrawing groups have been known for a long time, ketenes with both electron withdrawing and electron donating group are rare and information concerning their reactivities remains to be learned.⁵⁹

When acid chloride **13** was reacted with Et_3N in the presence of cyclopentadiene at -78°C , the product, **16**, was isolated in 46% yield. NMR spectra and X-ray crystallography confirmed the structure of **16**. Table 5 shows the ^1H NMR chemical shifts and their assignments for compound **16**.^{33,44,45,60}

Table 5. Proton Chemical Shift Assignments of **16**

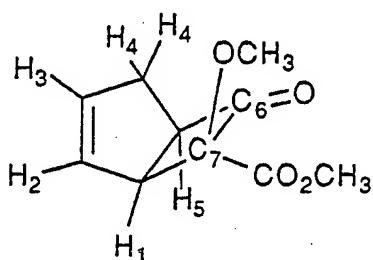
Chemical shift	H_1 and H_5	H_4	H_2 and H_3	Ester CH_3	OCH_3
δ	3.90	2.75 and 2.56	5.98 and 5.76	3.85	3.55
multiplicity	multiplet	multiplet	multiplet	singlet	singlet

Table 6 summarizes the ^{13}C NMR chemical shifts and their assignments for compound **16**. A proton off-resonance spectrum was used to determine the assignment and the results are also shown in Table 6.

Table 6. ^{13}C Chemical Shift Assignments of 16*

Chemical shift	C1 and C5	C2 and C3	C4	C6
δ	58.1 and 49.8	135.9 and 127.1	35.2	205.9
multiplicity**	doublet	doublet	triplet	singlet
Chemical shift	C7	OCH ₃	CO ₂ CH ₃	Ester C=O
δ	98.1	55.9	52.7	169.3
multiplicity**	singlet	quartet	quartet	singlet

* The atom numbers are shown as follow:



** From proton off-resonance decoupled spectra.

It is hard to determine the stereochemistry of the compound 16 from the NMR spectra alone, so an X-ray crystallographic study of compound 16 was performed by Professor Rasika Dias. The data are attached in appendices. Appendix VII shows the entire molecular structure as an ORTEP structure (Oakridge thermal ellipse program) including the stereochemical information for compound 16. Appendix VIII shows the bond lengths and bond angles of compound 16. Appendix IX shows the crystal data and data collection information. The structure shows that the methoxy group is in the endo-position and the methoxycarbonyl group is in the exo-position. The structure is not in agreement with the prediction given by the Woodward and Hoffmann rule for the ketene and cyclopentadiene

adducts. According to the mechanism, the large group, methoxycarbonyl, should be in the endo-position while the small group, methoxy, should be in the exo-position.

As has been stated earlier, there were exceptions to the stereochemistry of ketene and cyclopentadiene adducts from those predicted by the Woodward and Hoffmann rule. An example is 7-chloro-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one (7a) made by Ghosez and coworkers which also has the ester group in the exo- and chlorine in the endo-position. Incidentally, 7-chloro-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one bears the same ester group as compound 16. One possibility is that the ester group has a certain electronic influence on the transition state of the reaction as suggested by Goldstein et al.³² A possibly more reasonable explanation is as follows.

Unlike the other category of ketenes, α -acylketenes tends to form [2 + 4] cycloaddition products instead of [2 + 2] products when they react with alkenes. α -Acylketenes represent a 1,3-oxadiene system and alkenes act as dienophiles in this hetero-Diels-Alder reaction. The acyl group of the α -acylketenes can help the formation of charge separation in the transition state and can result a dipolar species,⁶¹ which will lead to the final product (Figure 8).

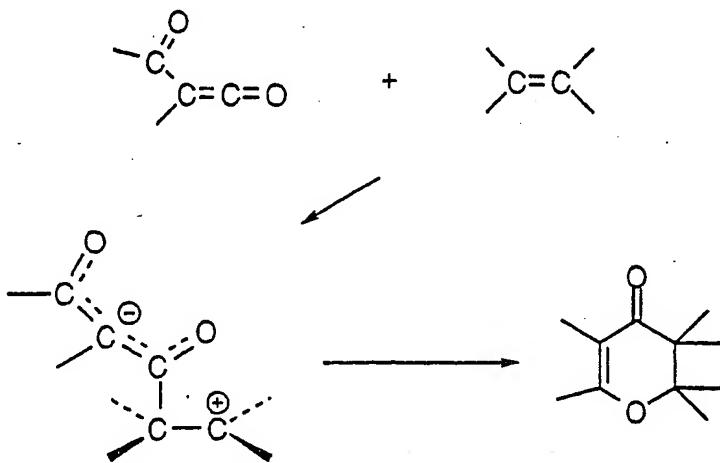


Figure 8. α -Acylketene and alkene addition

In the case of ketene **11** reacting with cyclopentadiene, the ketene also bears an acyl group. This can lead to a charge separation in the transition state long enough to produce a thermodynamically more stable product, that is the stereochemically less hindered isomer. It is obvious that the adjacent carbonyl group can stabilize the negative charge of the transition state.

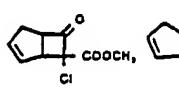
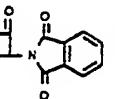
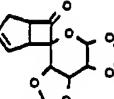
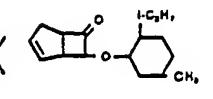
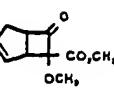
As has been pointed out earlier, reports on the stability of endo- versus exo-isomer of 7-monosubstituted bicyclo[3.2.0]hept-2-en-6-one were contradictory. But 7-methoxy-7-methoxycarbonylbicyclo[3.2.0]hept-2-ene-6-one is a disubstituted bicyclo[3.2.0]hept-2-en-6-one, the interaction of the groups on the 4-membered ring of bicyclo[3.2.0]hept-2-en-6-one could be different from 7-monosubstituted bicyclo[3.2.0]hept-2-en-6-one. It is very possible that **16** is the thermodynamically more stable product.

The reaction between ketene **11** and cyclopentadiene is quite possibly not a synchronous concerted cycloaddition. It may go through a zwitterionic intermediate, which leads to the thermodynamically more stable product.

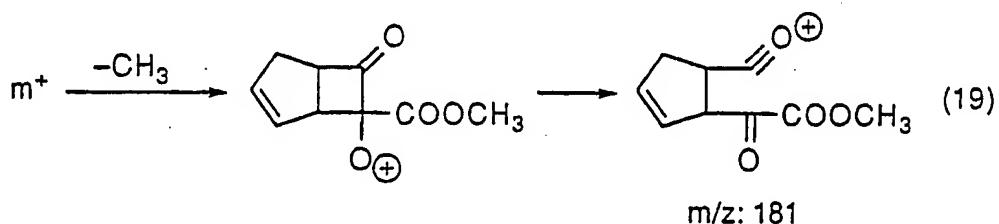
The bond lengths of 7-methoxy-7-methoxycarbonylbicyclo[3.2.0]hept-2-ene-6-one are shown in Table 7. The bond lengths of similar compounds are also listed in Table 7 for comparison. The atom numbers are the same as in Table 6.

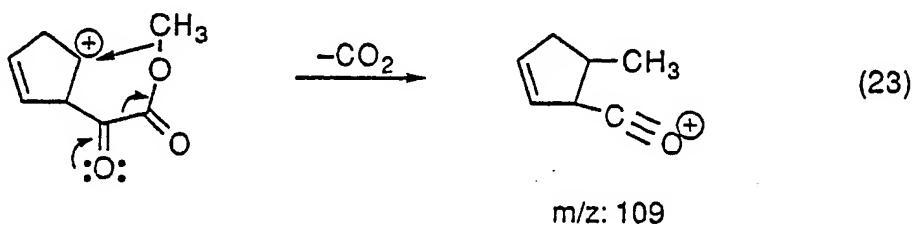
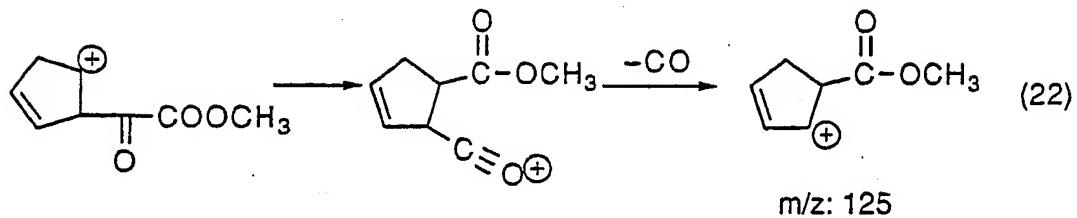
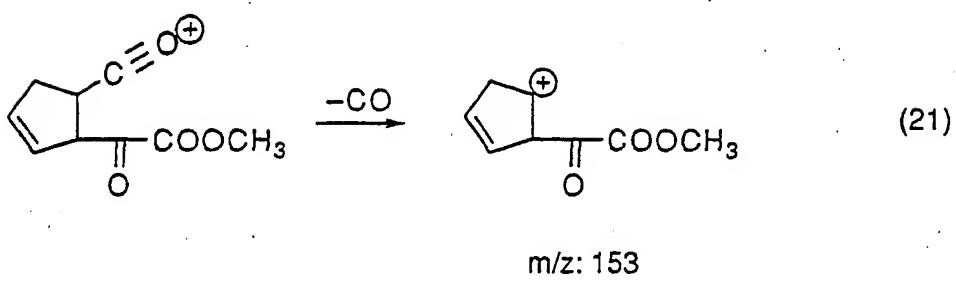
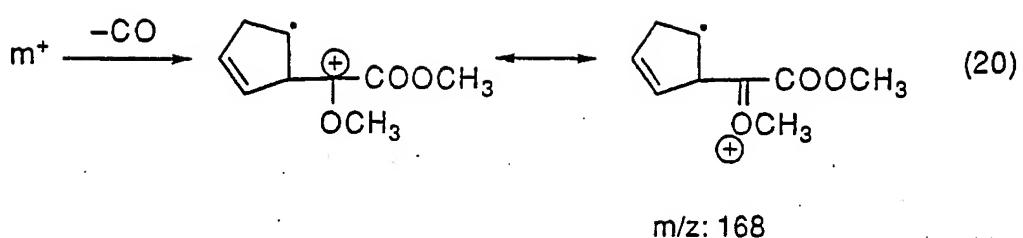
There are some interesting points about the data in Table 7. The carbon-carbon double bond and C3-C4 bond of compound **16** are significantly shorter than those of the similar compound, 7-chloro-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one while C6-C7 bond is significantly longer than that of 7-chloro-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one.

Table 7. Bond Length of Compound 16 and Other Similar Compounds

Bond Length (Å)					
C2-C3	1.337	1.322	1.327	1.318	1.317
C1-C2	1.505	1.510	1.500	1.495	1.495
C3-C4	1.523	1.522	1.492	1.504	1.488
C4-C5	1.543	1.516	1.556	1.528	1.534
C1-C5	1.560	1.565	1.566	1.560	1.556
C5-C6	1.510	1.520	1.518	1.531	1.504
C1-C7	1.572	1.541	1.566	1.568	1.565
C6-C7	1.528	1.543	1.556	1.519	1.559
Ref.	32	46	62	62	

Appendix V shows mass spectrum of compound 16. 196.1 is the m^+ peak. The 181.0 peak is from ($m\text{-CH}_3$) (equation 19); 168.1 is from ($m\text{-}28$) (equation 20); 153.0 is from ($m\text{-}43$) (equation 21); 125.1 is from ($m\text{-}71$) (equation 22); 109.1 from ($m\text{-}87$) (equation 23) and so on. The spectrum agrees with the structure of compound 16 very well.





CONCLUSION

Dimer **9** and dimer **10** which came from the thermal reaction of dimethyl diazomalonate were not produced by the reaction of the corresponding ketene **11**, methoxy(methoxycarbonyl)ketene and dimethyl diazomalonate under the conditions tried. The presence of methoxy(methoxycarbonyl)ketene was confirmed by the isolation of compound **16**, 7-methoxy-7-methoxycarbonylbicyclo[3.2.0] hept-2-ene-6-one, obtained by the in situ trapping of the ketene with cyclopentadiene. This, however, does not lead to the conclusion that the mechanism proposed in Scheme VIII and Scheme IX are not true. Further investigation is necessary to reach a more positive conclusion.

The ketene **11** and cyclopentadiene adduct, **16**, namely 7-methoxy-7-methoxycarbonylbicyclo[3.2.0] hept-2-ene-6-one, has a different stereochemistry from most of the other ketene and cyclopentadiene adducts but agrees with the stereochemistry of the adduct of $\text{H}_3\text{CO}_2\text{C}(\text{Cl})=\text{C=O}$ and cyclopentadiene. The mechanism of the formation of this adduct is considered to be in agreement with recent theoretical predictions.

EXPERIMENTAL

1. General

Infrared spectra were recorded on a Biorad-Digilab FTS-40 Fourier Transform Infrared instrument using powdered sample mixed with KBr in a diffuse reflectance unit or liquid samples between NaCl plates and reported as \bar{v} in cm^{-1} with 8 cm^{-1} resolution.

^1H NMR and ^{13}C NMR spectra were obtained on a Bruker MSL-300 spectrometer. ^1H NMR spectra were recorded at 300.13 MHz in CDCl_3 or D_2O and reported in ppm as δ relative to internal tetramethylsilane or the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid, respectively. ^{13}C NMR spectra were taken at 75.47 MHz in CDCl_3 or D_2O and are reported in ppm relative to the center peak of CDCl_3 at 77.00 ppm or the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid at 0.00 ppm, respectively.

HPLC was carried out using a Waters 501 HPLC pump, a Lambda-Max Model 481 LC UV-vis detector at 254 nm and Maxima 820 Chromatography Software with an ECONOSIL C18 reverse-phase column (250 mm x 4.6 mm) with a flow rate of 1 mL/min. GC chromatograms were recorded on a Varian model 3700 gas chromatograph with a silica capillary column of DB-5 (30 m long, 0.319 mm diameter, 0.025 μ coating thickness). The temperature program is 80 °C for one min. and a heating rate of 10 °C/min. from 80 °C to 240 °C.

X-ray crystallography was done on Siemens P4 instrument. The running temperature was kept at -40 °C due to the relatively low melting point of the compound. The mass spectrum was done on a Finnigan Mat TSQ70 instrument. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN analyzer. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Mg turnings were washed with diethyl ether and dried at 110 °C overnight. SOCl_2 , KOH, dimethyl methoxymalonate, dicyclopentadiene were used without further purification. Diethyl ether, THF and benzene were dried over sodium benzophenone ketyl radical and freshly distilled prior to use. CH_2Cl_2 and toluene were dried over 4A molecular sieve for 24 hours and freshly distilled prior to use.

2. Synthesis

Methyl 3-chloro-2-methoxy-3-oxopropanoate (13). 40.54 g (0.25 mol) of dimethyl methoxymalonate was dissolved in 100 mL of methanol, and 15.92 g (0.41 mol) of KOH was dissolved in 100 mL of methanol. The KOH solution was then added to the dimethyl methoxymalonate solution over 16 hours. After the addition, the reaction mixture was stirred at room temperature for 24 hours. No precipitate was observed. The methanol was removed under water aspirator vacuum and the residue was dried under vacuum (0.1 mm) overnight. A sticky and viscous liquid was obtained. This half hydrolysis product was used directly for the next step reaction without purification. ^1H NMR (in D_2O): δ : 4.25 (s), 3.66 (s), 3.26 (s); ^{13}C NMR (D_2O): δ : 174.7, 173.6, 84.9, 59.9, 55.4.

18 mL of thionyl chloride was added to the dry potassium salt product made above at 0 °C and the mixture was stirred at room temperature for 18 hours. Vacuum distillation three times gave a pure sample of 13. Overall yield 50%; b.p. 34-36 °C (0.50 mm). ^1H NMR: δ : 4.65 (s, 1H), 3.88 (s, 3H), 3.58 (s, 3H) (lit.^{63,64} ^1H NMR: δ : 4.65 (s, 1H), 3.85 (s, 3H), 3.58 (s, 3H)); ^{13}C NMR: δ : 168.9, 164.2, 86.7, 59.1, 53.5.

Dimethyl Diazomalonate (8). Dimethyl diazomalonate was prepared according to the literature procedure.⁵⁵ The yield was 90%; b.p. 52 °C at 0.05 mm Hg (lit.⁶⁵ b. p. 45 °C/0.2 mm). ^1H NMR: δ : 3.85; ^{13}C NMR: δ : 161.3, 65.6, 52.4.

Attempts to Prepare Dimers 9 and 10. All the reactions were done in a N₂ environment. 190 mg (1.2 mmol) of dimethyl diazomalonate (8) and 122 mg (1.28 mmol) of triethyl amine were charged into a 25 mL three-necked reaction flask and mixed with 10 mL of solvent. The mixture was kept under strictly dry conditions. Then 200 mg (1.3 mmol) of the acid chloride 13 in 5 mL of solvent was slowly added to the reaction mixture. The progress of the reaction was monitored by GC. After the acid chloride peak disappeared (about half an hour), the reaction mixture was filtered to remove the Et₃N-HCl. The solvent was removed under reduced pressure. The residue was dried under vacuum (0.01 mm Hg) overnight and then was used to run an NMR spectrum.

The reaction was run under 11 different sets of conditions:

1. Benzene as solvent, at 0 °C;
2. Benzene as solvent, at room temperature;
3. Benzene as solvent, at reflux;
4. CH₂Cl₂ as solvent, at 0 °C;
5. CH₂Cl₂ as solvent, at -78 °C;
6. THF as solvent, at 0 °C;
7. THF as solvent, at -78 °C;
8. Ether as solvent, at 0 °C;
9. Ether as solvent, at -78 °C;
10. Toluene as solvent, at room temperature;
11. Toluene as solvent, at reflux.

7-Methoxy-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one (16).

Cyclopentadiene was distilled by cracking dicyclopentadiene under a N₂ atmosphere into a flask cooled in a Dry-Ice bath right before use.

1.73 g (excess) of cyclopentadiene was mixed with 0.4 g (3.95 mmol) of Et₃N in 20 mL of dry ether. Then 0.56 g (3.36 mmol) of the acid chloride 13 in 5 mL of dry ether was slowly injected into the mixture under a N₂ atmosphere at -78 °C. A white salt precipitated out immediately. The reaction mixture was kept at -78 °C under the N₂ atmosphere for another half an hour and then was warmed to room temperature. The white salt was filtered and washed with 5 mL of cold ether. The liquid portion was then concentrated under reduced pressure. The residue was distilled under vacuum to give 0.3 g (yield 46%) of the product with b.p. at 61-63 °C (0.01 mm). An analytical sample was prepared by recrystallizing the distilled sample at -78 °C from hexanes. m.p. 57-58 °C. ¹H NMR: δ: 5.99-5.97 (m, 1H), 5.77-5.75 (m, 1H), 3.95-3.86 (m, 2H), 3.85 (s, 3H), 3.55 (s, 3H), 2.75 (m, 1H), 2.58-2.54 (m, 1H); ¹³C NMR: δ: 205.88, 169.29, 135.90, 127.08, 98.12, 58.12, 55.85, 52.73, 49.78, 35.24; MS: m/e: 196.1, 181.0, 168.1, 153.0, 125.1, 109.1, 93.0, 77.1, 66.1; IR: ̄: 3072, 3003, 2954, 2923, 2848, 1774, 1737, 1702, 1611, 1462, 1443, 1348, 1280, 1248, 1212, 1177, 1054, 1019, 988, 976, 926, 891, 833, 794, 775, 734, 666, 618, 579, 507 cm⁻¹; Anal. Calcd. for C₁₀H₂₁O₄: C, 61.22; H, 6.16. Found: C, 60.92; H, 5.86.

Preparation of the single crystal for X-ray crystallography. Crystals of 7-methoxy-7-methoxycarbonylbicyclo[3.2.0]hept-2-en-6-one were made as follows: A sample was dissolved in a small amount of hexanes at room temperature. The temperature of the solution was then reduced very slowly (15 °C/hr) using an acetone bath with slow addition of Dry-Ice to -78 °C. The single crystal formed had a feather-like structure and was ready for X-ray crystallography.

APPENDIX VI

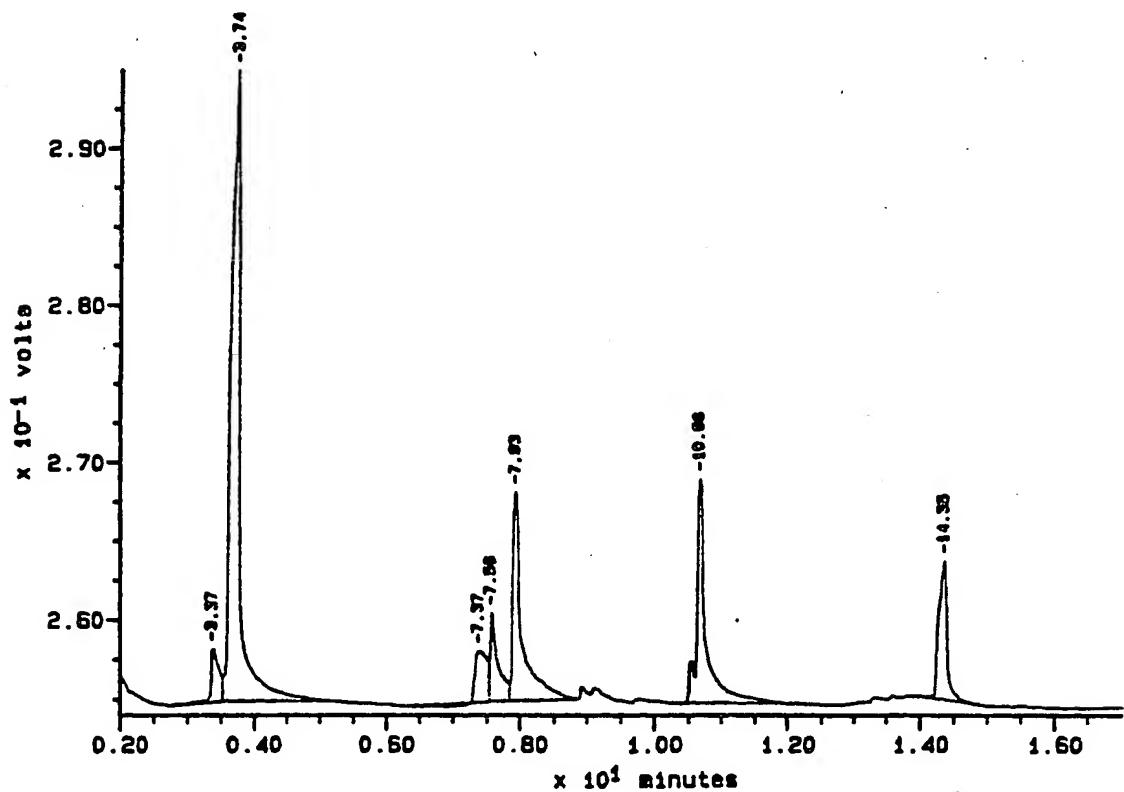
**GC CHROMATOGRAM OF THE REACTION BETWEEN METHYL
3-CHLORO-2-METHOXY-3-OXOPROPANOATE (13)
AND DIMETHYL DIAZOMALONATE 8
IN THE PRESENCE OF TRIETHYL-
AMINE IN REFLUXING
TOLUENE.**

Retention time of dimethyl diazomalonate 8: 3.7 minutes,

Retention time of methyl 3-chloro-2-methoxy-3-oxopropanoate (13): 2.9 minutes,

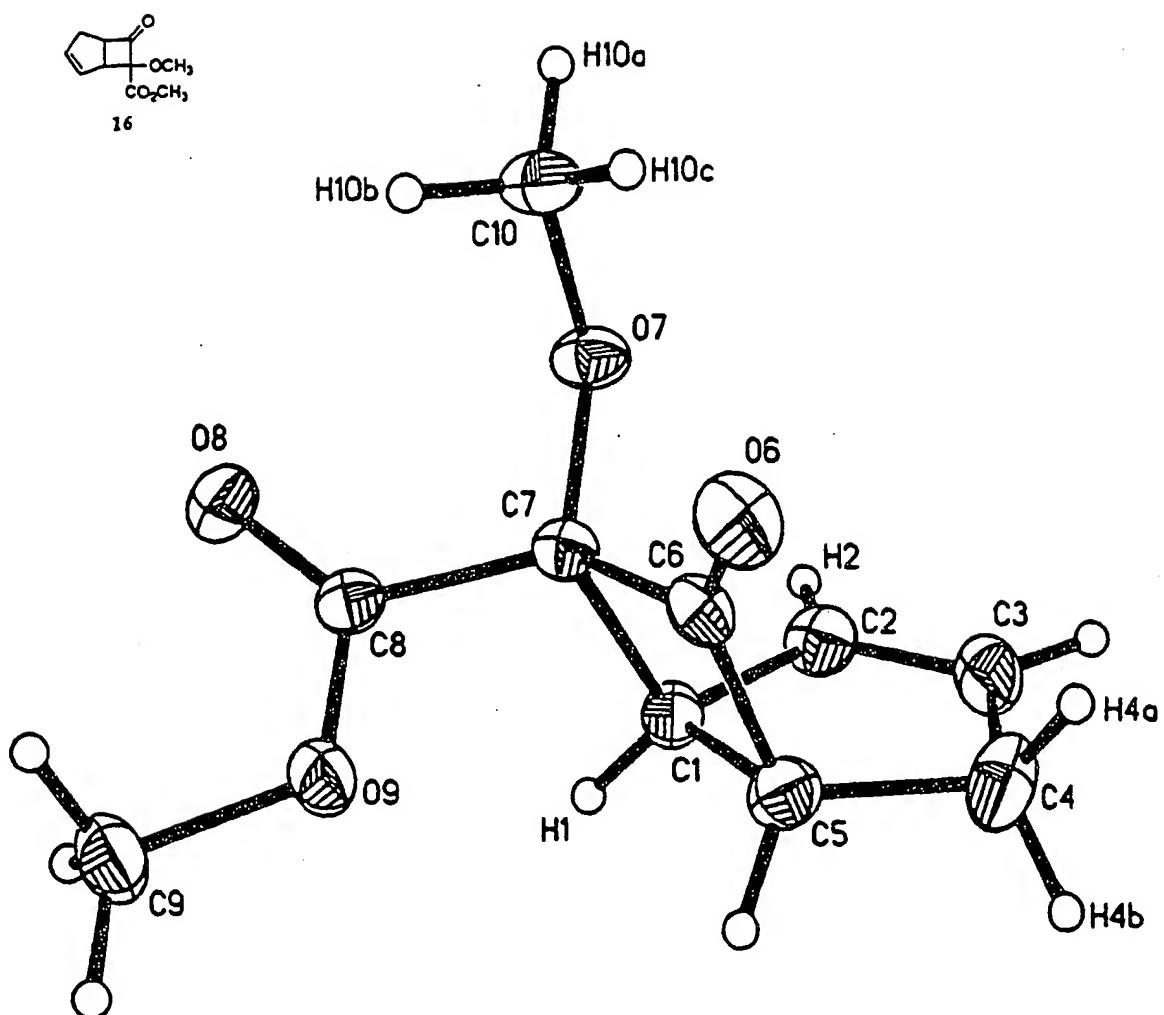
Retention time of dimer 9: 13.5 minutes,

Retention time of dimer 10: 11.7 minutes.



APPENDIX VII

**ORTEP STRUCTURE OF 7-METHOXY-7-METHOXY-
CARBONYLBICYCLO[3.2.0]HEPT-
2-EN-6-ONE (16).**



APPENDIX VIII

**BOND LENGTHS AND BOND ANGLES OF 7-METHOXY-7-
METHOXCARBONYLBICYCLO[3.2.0]HEPT-
2-EN-6-ONE (16)**

Bond lengths (\AA)

C(1)-H(1)	0.956	C(1)-C(2)	1.495 (3)
C(1)-C(5)	1.556 (3)	C(1)-C(7)	1.565 (3)
C(2)-H(2)	0.955	C(2)-C(3)	1.317 (4)
C(3)-H(3)	0.957	C(3)-C(4)	1.488 (4)
C(4)-H(4A)	0.956	C(4)-H(4B)	0.955
C(4)-C(5)	1.534 (3)	C(5)-H(5)	0.958
C(5)-C(6)	1.504 (4)	C(6)-O(6)	1.201 (3)
C(6)-C(7)	1.559 (3)	C(7)-O(7)	1.400 (3)
C(7)-C(8)	1.525 (3)	O(7)-C(10)	1.440 (3)
C(8)-O(8)	1.204 (3)	C(8)-O(9)	1.323 (3)
O(9)-C(9)	1.451 (3)	C(9)-H(9A)	0.957
C(9)-H(9B)	0.956	C(9)-H(9C)	0.955
C(10)-H(10A)	0.960	C(10)-H(10B)	0.960
C(10)-H(10C)	0.960		

Bond angles ($^{\circ}$)

H(1)-C(1)-C(2)	113.5(1)	H(1)-C(1)-C(5)	120.9(1)
C(2)-C(1)-C(5)	102.7(2)	H(1)-C(1)-C(7)	111.6(1)
C(2)-C(1)-C(7)	115.0(2)	C(5)-C(1)-C(7)	91.2(2)
C(1)-C(2)-H(2)	127.1(1)	C(1)-C(2)-C(3)	112.3(2)
H(2)-C(2)-C(3)	120.6(1)	C(2)-C(3)-H(3)	123.5(1)
C(2)-C(3)-C(4)	114.1(2)	H(3)-C(3)-C(4)	122.4(1)
C(3)-C(4)-H(4A)	110.8(2)	C(3)-C(4)-H(4B)	108.8(2)
H(4A)-C(4)-H(4B)	109.1(1)	C(3)-C(4)-C(5)	102.7(2)
H(4A)-C(4)-C(5)	109.2(1)	H(4B)-C(4)-C(5)	116.2(2)
C(1)-C(5)-C(4)	107.5(2)	C(1)-C(5)-H(5)	114.5(1)
C(4)-C(5)-H(5)	115.4(2)	C(1)-C(5)-C(6)	88.4(2)
C(4)-C(5)-C(6)	116.0(2)	H(5)-C(5)-C(6)	112.0(1)
C(5)-C(6)-O(6)	134.3(2)	C(5)-C(6)-C(7)	93.4(2)
O(6)-C(6)-C(7)	132.1(2)	C(1)-C(7)-C(6)	86.1(2)
C(1)-C(7)-O(7)	113.4(2)	C(6)-C(7)-O(7)	117.1(2)
C(1)-C(7)-C(8)	112.6(2)	C(6)-C(7)-C(8)	113.4(2)
O(7)-C(7)-C(8)	111.9(2)	C(7)-O(7)-C(10)	114.6(2)
C(7)-C(8)-O(8)	124.7(2)	C(7)-C(8)-O(9)	110.6(2)
O(8)-C(8)-O(9)	124.8(2)	C(8)-O(9)-C(9)	116.8(2)
O(9)-C(9)-H(9A)	114.5(1)	O(9)-C(9)-H(9B)	105.6(1)
H(9A)-C(9)-H(9B)	109.4(1)	O(9)-C(9)-H(9C)	108.3(1)
H(9A)-C(9)-H(9C)	109.3(1)	H(9B)-C(9)-H(9C)	109.6(1)
C(7)-C(10)-H(10A)	109.5(1)	O(7)-C(10)-H(10B)	109.5(1)
H(10A)-C(10)-H(10B)	109.5(1)	O(7)-C(10)-H(10C)	109.5(1)
H(10A)-C(10)-H(10C)	109.5(1)	H(10B)-C(10)-H(10C)	109.5(1)

APPENDIX IX

CRYSTAL DATA AND DATA COLLECTION INFORMATION OF 7-METHOXY-7-METHOXCARBONYLBICYCLO[3.2.0]HEPT-2-EN-6-ONE (16)

STRUCTURE DETERMINATION SUMMARYCrystal Data

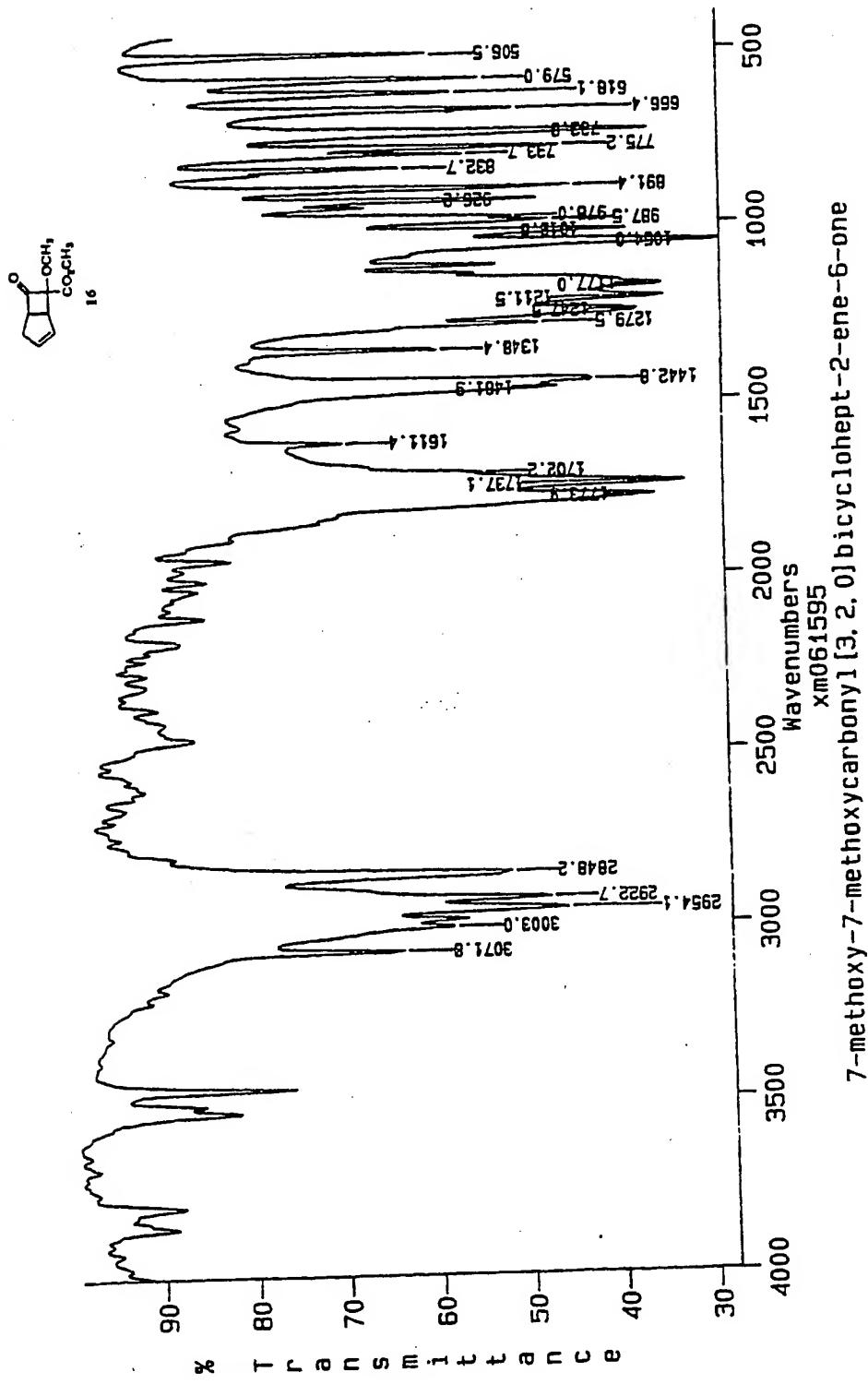
Empirical Formula	C ₁₀ H ₁₂ O ₄
Color; Habit	Colorless Blocks
Crystal size (mm)	0.47 x 0.50 x 0.61
Crystal System	Triclinic
Space Group	P ⁻ 1
Unit Cell Dimensions	$a = 6.2340(10) \text{ \AA}$ $b = 7.1750(10) \text{ \AA}$ $c = 12.0320(10) \text{ \AA}$ $\alpha = 76.190(10)^\circ$ $\beta = 87.290(10)^\circ$ $\gamma = 68.260(10)^\circ$
Volume	484.89(11) \AA^3
Z	2
Formula weight	196.2
Density(calc.)	1.344 Mg/m ³
Absorption Coefficient	0.104 mm ⁻¹
F(000)	208

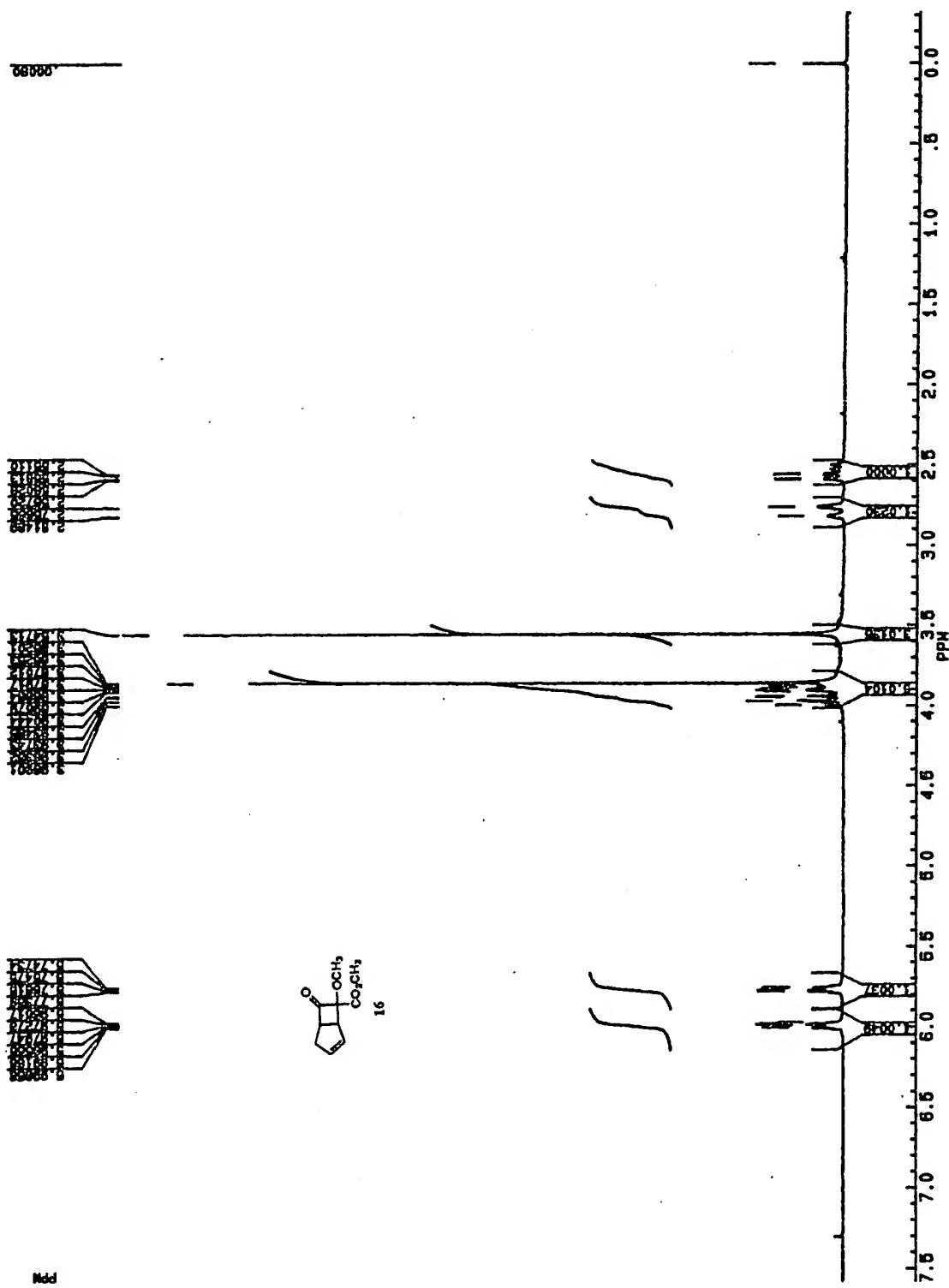
Data Collection

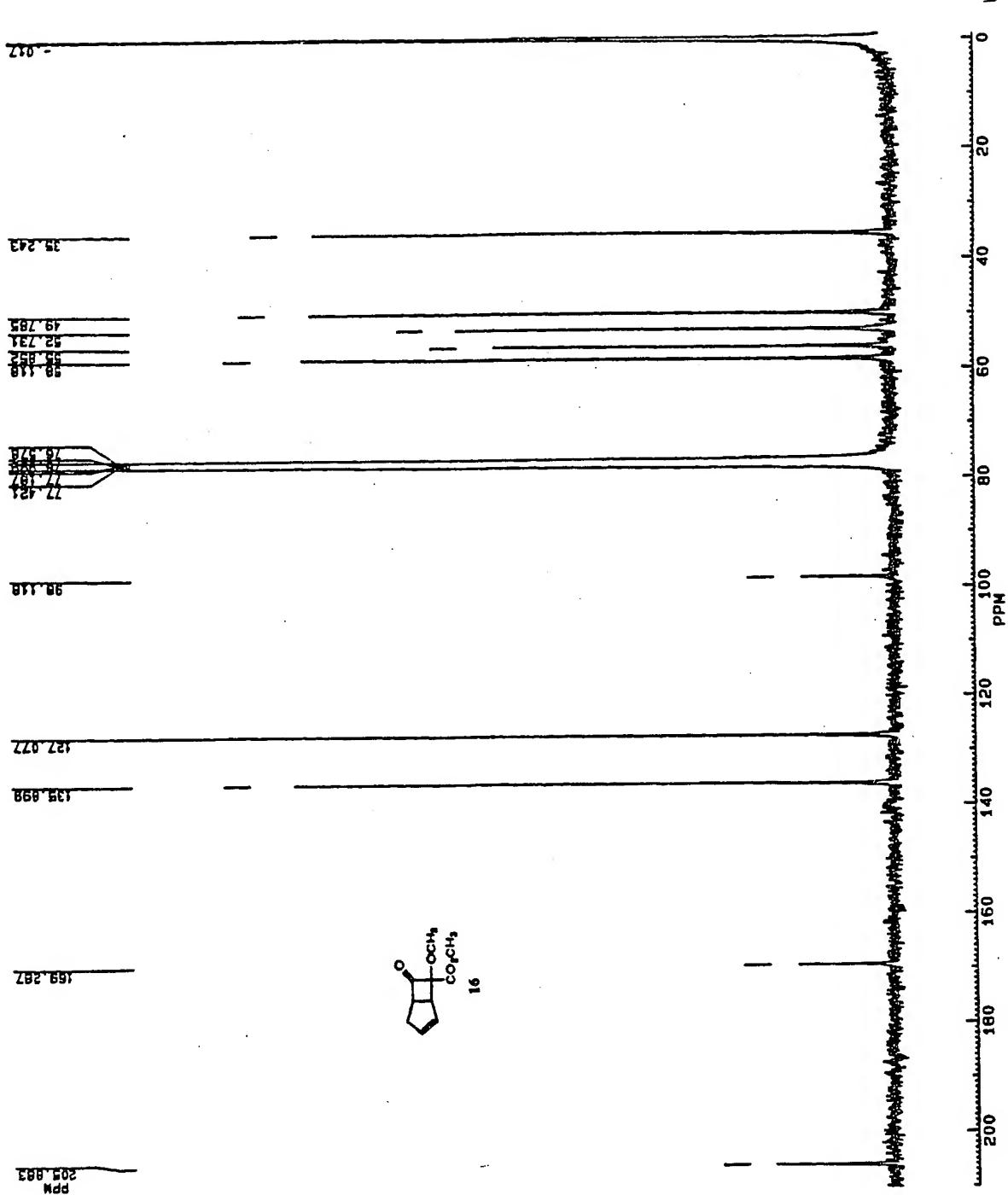
Diffractometer Used	Siemens RP4
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
Temperature (K)	233
Monochromator	Highly oriented graphite crystal
2θ Range	3.5 to 45.0°
Scan Type	2θ-θ
Scan Speed	Variable; 3.00 to 45.00°/min. in ω
Scan Range (ω)	0.70° plus $K\alpha$ -separation
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-1 \leq h \leq 6, -7 \leq k \leq 7$ $-12 \leq l \leq 12$
Reflections Collected	1668
Independent Reflections	1255 ($R_{\text{int}} = 4.09\%$)
Observed Reflections	1047 ($F > 4.0\sigma(F)$)
Absorption Correction	N/A

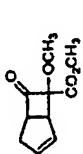
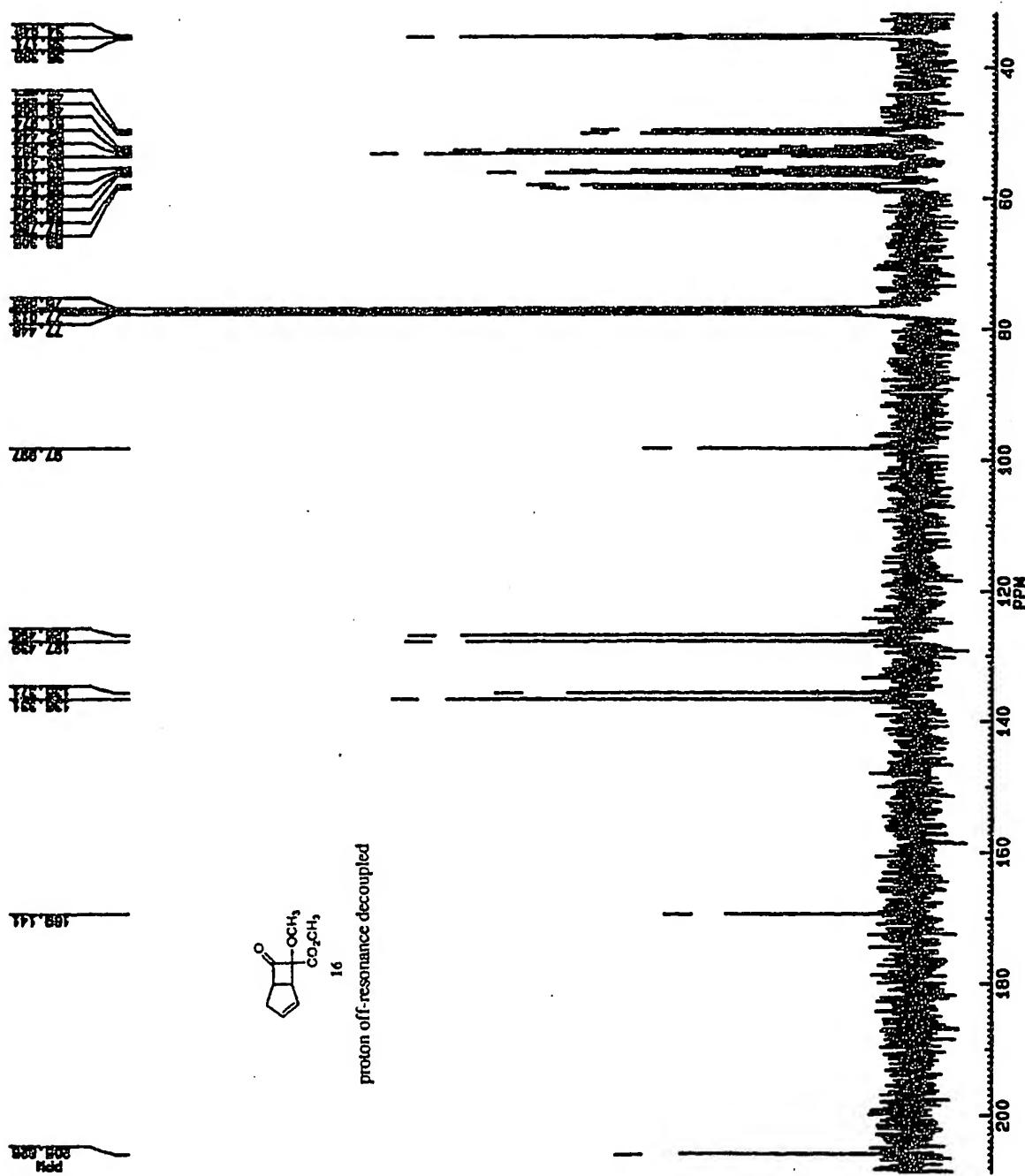
APPENDIX X

IR, NMR AND MASS SPECTRA OF 7-METHOXY-7-METHOXCARBONYL-
BICYCLO[3.2.0]HEPT-2-EN-6-ONE (16)

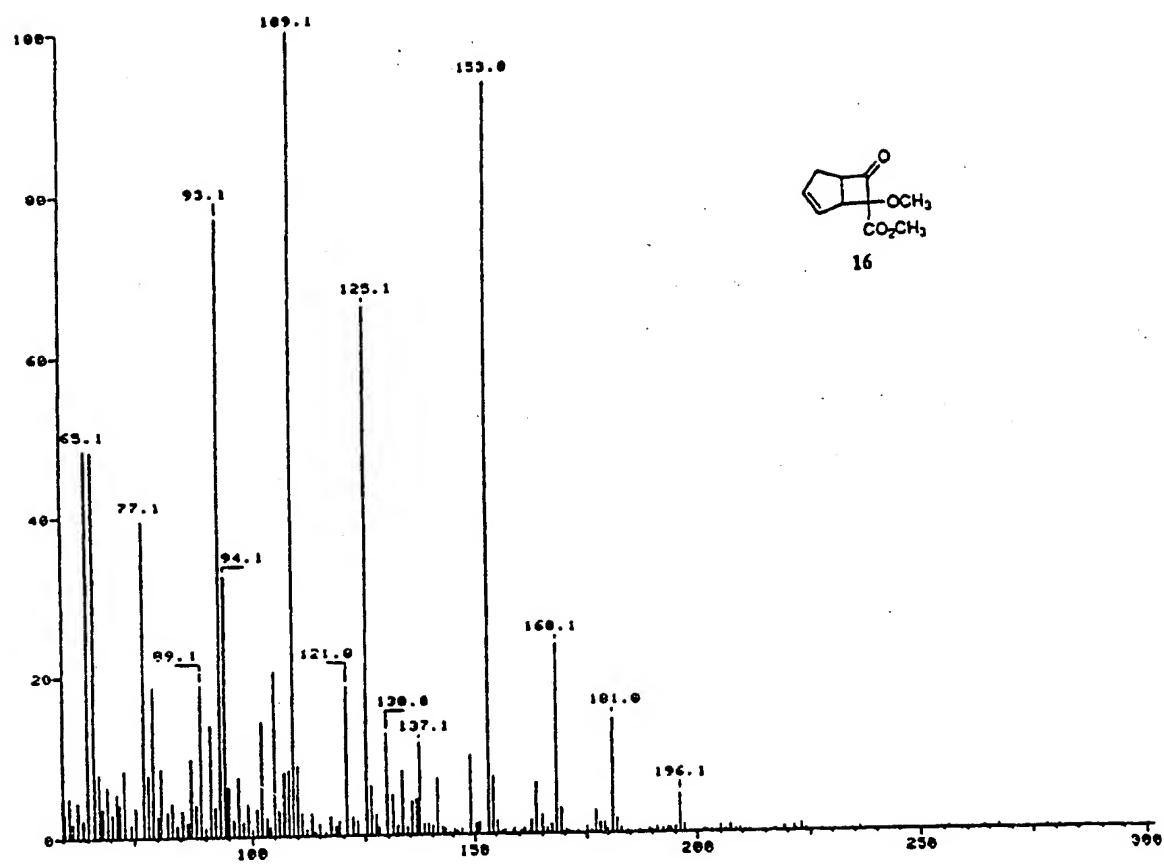








proton off-resonance decoupled



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